THERMODYNAMICS

AN ADVANCED TREATMENT FOR CHEMISTS AND PHYSICISTS

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FOR CHEMISTS AND PHYSICISTS

by

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IMPORTANT SYMBOLS

A affinity
A area
B second virial coefficient
C or C_P heat capacity at constant pressure
C_V heat capacity at constant volume
E electromotive force
F free energy or Helmholtz function
F Faraday
G Gibbs function
H heat function
I moment of inertia
I ionic strength
J Massieu function
K equilibrium constant
L Avogadro's number
M molar mass
N number of molecules or photons
P pressure
$P^\dagger$ standard pressure, e.g. one atmosphere
Q electric charge
R gas constant
S entropy
T absolute temperature
U energy
V volume
Y Planck function

B   magnetic force vector (induction)
D   electric derived vector (displacement)
E   electric force vector (field)
H   magnetic derived vector (field)
J   current density

M	magnetization
P	electric polarization
a	relative activity
a	radiation density constant
c	speed of light
c	volume concentration
e	charge of proton
f	activity coefficient related to ideal mixture
g	statistical weight
g	gravitational acceleration
h	Planck's constant
i	electric current
k	Boltzmann's constant
l	distribution coefficient
m	molality
m	mass of molecule
n	number of moles
p	partial vapour pressure
p*	fugacity
q	heat absorbed by system
r	mole ratio
r	radius
s	solubility
t	transport number
w	work done on system
w	mass fraction
x	mole fraction
z	charge number of ion
α	relative volatility
α	coefficient of thermal expansion
α	constant in Debye's limiting law
β	ionic specific interaction coefficient
$\boldsymbol{\beta}$	Bohr's magneton
γ	surface tension
γ	activity coefficient of solute related to ideal dilute solution
ε	energy of individual molecule or photon
ε	permittivity
$\varkappa$	compressibility
λ	absolute activity

μ	chemical potential or ionic electrochemical potential
μ	permeability
μ	electric moment of molecule
ν	stoichiometric number
ν	frequency
ξ	extent of reaction
o	orientational weight
ϱ	density
ϱ	radius of curvature
σ	symmetry number
τ	thickness of interfacial layer
φ	osmotic coefficient
φ	volume fraction
ψ	electrical potential
Γ	surface concentration
Θ	characteristic temperature
Π	osmotic pressure
Φ	gravitational potential

Subscripts often refer to component species, e.g. p_i is the partial vapour pressure of the component species i. In particular

1	solvent
s	solute
i	especially to ionic species
R	cation
x	anion
m	mean molar
φ	apparent molar of solute

Subscripts attached to the operator symbol Δ refer to processes as follows

e	evaporation
f	fusion
s	sublimation
$\alpha \to \beta$	transfer from phase α to phase β

Superscripts usually refer to phases, e.g. p_i^α is the partial vapour pressure of the species i in the phase α. In particular

α, β	bulk phases
σ	surface phase
G	gas
L	liquid
S	solid
0	pure substance
I	ideal mixture
E	excess over ideal mixture
id	ideal dilute solution
∞	standard value with mole ratios
$\ominus$	standard value with molalities

A star is used to distinguish the fugacity p^* from the partial vapour pressure p.

A dagger is used in the symbol $P^\dagger$ to denote a standard pressure, e.g. one atmosphere. Attached to other symbols, e.g. μ, it denotes a standard value independent of the pressure.

The following operator signs are used

d	ordinary differential
$\dfrac{\partial}{\partial}$	partial differential coefficient
D	differential at varying composition, but constant temperature and constant pressure
Δ	excess of final over initial value
Σ	summation
$\int$	integral
Π	product
$\Pi\,(\,)$	product referring to species on right of chemical formula divided by product referring to species on left
[ ]	average between two temperatures or two pressures, usually one relating to a solution the other to the pure solvent
ln	natural logarithm
log	logarithm to base 10

VALUES OF SOME PHYSICAL CONSTANTS *

Ice-point	T_{ice}	$= 273.15$	$°K$
Avogadro's number	L	$= 0.60236 \times 10^{24}$	$mole^{-1}$
Atmosphere	1 atm	$= 1.01325 \times 10^6$	$dyne\ cm^{-2}$
		$= 1.01325 \times 10^5$	$J\ m^{-3}$
Thermochemical calorie	1 cal	$= 4.1840$	J
Gas constant	R	$= 8.3147$	$J\ deg^{-1}\ mole^{-1}$
	RT_{ice}	$= 2271.16$	$J\ mole^{-1}$
Boltzmann's constant	$k = R/L$	$= 1.3803 \times 10^{-16}$	$erg\ deg^{-1}$
Planck's constant	h	$= 6.625 \times 10^{-27}$	$g\ cm^2\ s^{-1}$
Faraday	F	$= 0.96497 \times 10^5$	$C\ mole^{-1}$
Proton charge	$e = F/L$	$= 1.6020 \times 10^{-19}$	C
Speed of light	c	$= 2.9979 \times 10^8$	$m\ s^{-1}$
Bohr's magneton	β	$= 9.273 \times 10^{-24}$	$A\ m^2$
	$L\beta$	$= 5.586$	$A\ m^2\ mole^{-1}$

* Stille, *Messen und Rechnen in der Physik* 1955

INTRODUCTION CONCERNING NOTATION

We shall consistently use symbols to denote physical quantities, not their measure in terms of particular units. For example, we may write of a pressure P

$$
\begin{aligned}
P &= 1.2 \text{ atm} \\
&= 91.2 \text{ cm Hg} \\
&= 0.912 \text{ m Hg} \\
&= 1.216 \times 10^6 \text{ dyne cm}^{-2} \\
&= 0.1216 \text{ J cm}^{-3} \\
&= 1.216 \times 10^6 \text{ g cm}^{-1} \text{ s}^{-2}
\end{aligned}
$$

or alternatively $P/\text{atm} = 1.2$ but under no circumstances shall we equate P to 1.2 or any other number. This method of notation sometimes called "equations of quantities" and sometimes "quantity calculus" is far from new. It was recommended by Alfred Lodge.[*] It has been used by some of the greatest theoretical physicists, in particular Planck and Sommerfeld, but not generally in England. The advantages of this notation have been emphasized by Henderson[†] who attributed it to Stroud.

This notation is especially clear and tidy for labelling the axes of a graph, e.g.

$\log (p/\text{atm})$ rather than $\log p \ (\text{atm})$

$10^3 \text{ deg}/T$ $1/T \ (\text{deg}) \times 10^3$

So far as possible we adhere in our notation to the recommendations of the International Union of Pure and Applied Chemistry (1949, 1955)

[*] *Nature* 1888 **38** 281.
[†] *Math. Gaz.* 1924 **12** 99.

and the International Union of Pure and Applied Physics (1955), these being in almost complete mutual agreement. In particular we use italic (sloping) letters for symbols for physical quantities and roman (upright) letters for abbreviations of units.

After reflection and with regret we are unable to use an internationally recommended symbol for Avogadro's number. For such an important constant a single letter in ordinary type is desirable. The symbol N is required for number of molecules together with n for number of moles. For the ratio N/n a different letter is needed. The choice of L has at least the following merits. In the first place the symbol L has but few other uses and none related to Avogadro's number. Secondly, although not internationally recommended, L is generally used in some countries and has been used by some eminent English-speaking physicists.[*] Thirdly L is the initial of Loschmidt who first considered the value of the number called in English Avogadro's number and in German Loschmidtsche Zahl.

We use ln to denote natural logarithm and log to denote common (decadic) logarithm.

We of course use the symbols °C and °K to denote the values of a temperature on the Celsius and Kelvin scales respectively, but the centigrade degree, the unit of interval on either of these scales, will be denoted by the abbreviation deg. Thus we write for the heat capacity of water

$$C = 4.1793 \text{ J g}^{-1} \text{ deg}^{-1} \text{ at } 25 \text{ °C}$$

The most convenient unit of quantity for a given species in physical chemistry is the mole. We shall use this unit not only for ordinary molecular species but also for atomic species, ionic species, and free radicals. We accordingly adopt the following definitions.

Avogadro's number is the number of atoms in 16 grams of oxygen. The mole is a measure of quantity equal to this number of molecules or atoms or ions or radicals as the case may be [†].

The question arises whether the mole should be mentioned explicitly in the names of units related to the mole. This is a question of convention and we are free to choose our answer provided we are consistent. We have come to the conclusion that it is convenient to mention the

[*] Compare Van Vleck, *Electric and Magnetic Susceptibilities* 1932.

[†] Compare Sillén, Lange and Gabrielson, *Problems in Physical Chemistry* 1952 p. 1.

mole, but not the molecule, in the names of units. Thus of the three alternatives

(a) $L = 0.602 \times 10^{24}$

(b) $L = 0.602 \times 10^{24}$ molecule mole^{-1}

(c) $L = 0.602 \times 10^{24}$ mole^{-1}

we choose the last.*

In accordance with this convention we should write

$$k = 1.380 \times 10^{-16} \text{ erg deg}^{-1} \quad \textit{not} \text{ erg deg}^{-1} \text{ molecule}^{-1}$$

but $R = 8.315$ J deg^{-1} mole^{-1} *not* J deg^{-1}

$e = 1.602 \times 10^{-19}$ C   *not* C ion^{-1}

but   F $= 0.965 \times 10^5$ C mole^{-1} *not* C

The quantity conventionally called "molecular weight" is defined as the ratio of the molar mass to one sixteenth the molar mass of O or as the ratio of the molar mass to one thirty-second of the molar mass of O_2. Thus the so-called "molecular weight" is neither a weight nor a mass but a numerical ratio. For the sake of consistency we shall state, for example, that the molar mass of N_2 is 28 g mole^{-1}.

Corresponding to each extensive property such as volume, energy, etc., there is a specific quantity which we define as the (extensive) property per unit quantity. We consider it unnecessary to have a different name or a different symbol for different units of quantity. For example the specific volume of water is 1 ml g^{-1} or 18 ml mole^{-1} or 0.1 gal lb^{-1}, and for the heat capacity (at constant pressure) C_P of gaseous nitrogen we write

$$C_P = 1.04 \text{ J deg}^{-1} \text{ g}^{-1} = 29.1 \text{ J deg}^{-1} \text{ mole}^{-1}$$

We shall apply the same considerations to the partial quantities introduced in chapter 5.

INTRODUCTION AND FUNDAMENTAL PRINCIPLES

§ 1. 01 THERMODYNAMICS OR THERMOPHYSICS

The word *thermodynamics* is a misleading name. This, possibly surprising statement, will now be elaborated.

Consider as a typical example of a mechanical system a heavy weight suspended by a spring of comparatively negligible weight. Such a system has a characteristic frequency determined by the magnitude of the weight, the dimensions and material of the spring. But that is not all. In general the characteristic frequency varies according as the spring is hot or cold. This variation can be related to the energy that has to be supplied to the spring to prevent it from becoming hotter or colder when compressed or extended. The quantitative study of such relations would reasonably be called *thermo-mechanics* or perhaps *thermo-dynamics*.

Again, consider a simple compressible fluid. Its compressibility in general depends on the pressure and on the nature of the fluid. But that is not all. It also generally varies according as the fluid is hot or cold. This variation can be related to the energy that has to be supplied to the fluid to prevent it from becoming hotter or colder when compressed. The quantitative study of such relations would reasonably be called *thermo-hydrodynamics*.

Again, consider a parallel plate condenser immersed in a uniform liquid. The capacity of such a condenser depends on the size and spacing of the plates and on the nature of the liquid, but it also in general varies according as the liquid is hot or cold. This variation can be related to the energy that has to be supplied to the liquid to prevent it from becoming hotter or colder when the condenser is charged or discharged. The quantitative study of such relations would reasonably be called *thermo-electrostatics*. (The word *thermo-electricity* has a different meaning.)

Again, consider a transformer consisting of two co-axial coils of insulated copper wire, the whole completely immersed in a solution of

a ferric salt. The mutual inductance of the transformer depends on the geometry of the two coils and on the composition of the ferric salt solution, but it also varies according as the solution is hot or cold. This variation can be related to the energy that has to be supplied to the solution to prevent it from becoming hotter or colder when the primary circuit is made or broken. The quantitative study of such relations would reasonably be called *thermo-electrodynamics* or *thermo-magnetics*.

As a last example consider the chemical system consisting of a gaseous mixture of hydrogen, nitrogen and ammonia in the presence of an efficient catalyst. The equilibrium quantity of ammonia depends on the total quantities, combined or free, of hydrogen and nitrogen and on the pressure, but it also varies according as the mixture is hot or cold. This variation can be related to the energy that has to be supplied to the mixture to prevent it from becoming hotter or colder during the chemical synthesis or decomposition of ammonia. The quantitative study of such relations would reasonably be called *thermo-chemics*. (The word *thermochemistry* is generally used in a much more restricted sense.)

We have now seen what might reasonably be called *thermo-mechanics* (or *thermo-dynamics*), *thermo-hydrodynamics*, *thermo-electrostatics*, *thermo-electrodynamics* (or *thermo-magnetics*) and *thermo-chemics*. These examples are not exhaustive. For example we could reasonably define *thermo-capillarity* and *thermo-acoustics*. The natural and obvious name for the science which embraces all these classes is *thermophysics*. Unfortunately the name *thermodynamics* is used instead. Its use is so firmly established, that it would probably be futile to suggest a change of name. It does however seem worth while stressing that this science, whether called *thermophysics* or not, does in fact have a bearing on nearly all branches of physics, as well as chemistry.

§ 1. 02 METHOD OF TREATMENT

Thermodynamics, like classical mechanics and classical electromagnetism, is an exact mathematical science. Each such science may be based on a small number of premises or laws from which all the remaining laws of the science are deducible by purely logical reasoning. In the case of each of these sciences there is a certain amount of arbitrariness as to which of the laws one chooses as the premises from which the others are to be deduced.

In classical mechanics, for instance, one might begin with Newton's laws of motion or alternatively one might use as the basis of the whole

theory the principle of least action. For an elementary exposition of the subject it is customary to choose the former, but to a reader already comparatively familiar with the subject the latter choice might be more satisfying. Whichever basis one chooses for the development of the theory this basis postulates the existence and definiteness of certain measurable quantities. In the one case they may be distance, time, mass and force, in the other generalized co-ordinates, generalized momenta, time and energy. There is a common tendency to regard the conceptions of mass and force as more fundamental than those of generalized momenta and energy, and therefore to regard them as more natural "bricks" with which to build up the complete structure of classical mechanics. But surely this is begging the question. When we first learn the elements of mechanics we always do, in fact, commence by using mass and force as the "bricks". As a consequence of this they are the more familiar "bricks" and so, without pausing to think why they are more familiar, we are apt to regard them as the natural ones. Actually if we analyse the claim of mass to priority over energy and momentum, we find it due to the accidental fact that we live in a very nearly constant gravitational field, as a consequence of which the mass of a body is proportional to its weight and so is readily measured with a common weighing machine. Newton's laws may be the best starting point in the elementary teaching of classical mechanics, but the complete theory can be built up on other bases which, from a logical point of view, are at least equally firm. They may be less satisfactory practically but more so intellectually.

Similarly the classical theory of electromagnetism is still usually built up from conceptions such as electric and magnetic poles. Whether or not this choice is desirable for a first introduction to the subject, there are undoubtedly other more solid "bricks" from which to build the structure in an advanced treatment, such as for example the "four-potential" and "four-current" of the special relativity theory.

In the case of thermodynamics the situation is no different. It is customary to regard *temperature*, the measure of hotness, as a natural "brick" and *entropy*, the measure of direction of change, as an unnatural one. This attitude is due to a feeling that temperature is more directly measurable. If, however, we analyse the question of how to measure temperature, we find a choice of two answers, neither of which is satisfactory: —

1. Measure it anyhow with any kind of "thermometer". We then obtain clumsy unnatural scales of temperature.

2. Measure it by means of a particular type of thermometer involving the use of a special kind of substance called a *perfect gas*. We thus obtain a convenient and natural temperature scale known as the absolute scale. But if we ask what is a *perfect gas* and by what criterion are we to recognize one, the only answer obtainable without leaving the province of thermodynamics is that a *perfect gas* is a substance with certain properties, the most important of which is that when used as a thermometer it gives the convenient and natural temperature scale.

This kind of basis for an exact mathematical science is deplorable. The apparent vicious circle is due to an unconscious attempt to build up the structure without having chosen the right "bricks". The usual introduction to entropy is unsatisfactory. For it is made dependent on the absolute temperature, a definition of which, independent of the postulate that certain substances make more perfect thermometers than others, involves conceptions, such as that of a Carnot cycle, which are at least as complex as the conception of entropy itself.

We have deliberately chosen to regard *absolute temperature* and *entropy*, just as we regard pressure and volume, as two quantities both fundamental. We therefore do not attempt to define them in terms of other quantities regarded as simpler, for we do not admit the existence of simpler thermodynamic quantities. Nor do we attempt to define the one in terms of the other because we regard them as equally fundamental. We define them merely by their properties, expressed either in words or by mathematical formulae.

§ 1. 03 THERMODYNAMIC STATE. PHASES

The simplest example of a system to which thermodynamics can be applied is a single homogeneous substance. In this simplest case a complete description of its thermodynamic state requires a specification of its content, i.e. quantity of each chemical substance contained, and further a specification of two other quantities such as for example volume and viscosity, or density and pressure. If all the physical properties of the system in which we are interested were independent of whether the system is hot or cold, it would in order to describe its state be sufficient to specify, apart from the quantity of each chemical substance contained, only one quantity, such as volume. Usually some, if not all, of the properties of interest do depend on whether the body is hot or cold and the specification of one extra independent quantity fixes the degree of hotness or coldness. Thus this simple

thermo-hydrodynamic system has one more degree of freedom than the corresponding *hydrodynamic* system.

If the system is not homogeneous, in order to describe its thermodynamic state we have to consider it as composed of a number, small or large, of homogeneous parts called *phases* each of which is described by specifying its content and a sufficient number of other properties; the sufficient number for each *thermo-physical* phase is always one more than in the corresponding hypothetical *physical* system with all its properties of interest independent of whether it is hot or cold.

In some cases the complete description of the thermodynamic state of a system may require it to be regarded as composed of an infinite number of infinitesimal phases. If the physical properties vary continuously over macroscopic parts of the system, this procedure offers no difficulty. An example is a high column of gas in a gravitational field. If on the other hand there are infinitely many discontinuities over finite regions, it may be difficult if not impossible to give a complete description of the thermodynamic state. An example is a gas flowing turbulently through an orifice.

In considering the properties of interfaces, we shall have to include phases which are extremely thin in the direction normal to the interface.

To sum up, the complete description of the thermodynamic state of any system involves a description of the thermodynamic state of each of its homogeneous phases, which may be few or many or infinite in number. The description of the thermodynamic state of each phase requires the specification of one more property than the description of the physical state of an analogous hypothetical phase all of whose properties of interest are independent of whether it be hot or cold.

§ 1. 04 THERMODYNAMIC PROCESS

If on comparing the state of a thermodynamic system at two different times it is found that there is a difference in any macroscopic property of the system, then we say that between the two times of observation a *process* has taken place. If, for example, two equal quantities of gas are allowed to intermix, this will constitute a *process* from a thermodynamic point of view provided the two initially separate gases are distinguishable by any macroscopic property, even though their difference is very slight, as, for example, might be the case for two isotopes. If, on the other hand, the two initially separate gases are not distinguishable by any macroscopic property, then from a

thermodynamic point of view no *process* takes place, although from a molecular standpoint there is a never-ceasing intermixing.

§ 1. 05 INFINITESIMAL PROCESS

A process taking place to such an extent that there is only an infinitesimal change in any of the macroscopic properties of a system is called an *infinitesimal process*.

§ 1. 06 INSULATING WALLS. ADIABATIC PROCESSES

The boundary or wall separating two systems is said to be *insulating* if it has the following property. If any system in complete internal equilibrium is completely surrounded by an *insulating* wall then no change can be produced in the system by external agency except by

(*a*) movement of the containing wall or part of it

(*b*) long range forces, e.g. movement of electrically charged bodies. When a system is surrounded by an insulating boundary the system is said to be *thermally insulated* and any process taking place in the system is called *adiabatic*. The name adiabatic appears to be due to Rankine *.

§ 1. 07 CONDUCTING WALLS. THERMAL EQUILIBRIUM

The boundary or wall separating two systems is said to be *thermally conducting* if it has the following property. If any two separate systems each in complete internal equilibrium are brought together so as to be in contact through a *thermally conducting* wall then in general the two systems will be found not to be in mutual equilibrium, but will gradually adjust themselves until eventually they do reach mutual equilibrium after which there will of course be no further change. The two systems are then said to have reached a state of *thermal equilibrium*. It was necessary to include the words "in general" in the definition to allow for the exceptional case that the two systems were already in thermal equilibrium. Systems separated by a conducting boundary are said to be in *thermal contact*.

§ 1. 08 ZEROTH PRINCIPLE. TEMPERATURE

We are now ready to formulate one of the important principles of thermodynamics.

If two systems are both in thermal equilibrium with a third system then they are in thermal equilibrium with each other.

* See Maxwell, *Theory of Heat* 1871 ed. p. 129.

This will be referred to as the *zeroth principle* of thermodynamics.

Consider now a reference system in a well defined state. Then all other systems in thermal equilibrium with it have a property in common, namely the property of being in thermal equilibrium with one another. This property is called *temperature*. In other words systems in *thermal equilibrium* are said to have the *same temperature*. Systems not in thermal equilibrium are said to have different temperatures.

§ 1. 09 THERMOSTATS AND THERMOMETERS

Consider two systems in thermal contact, one much smaller than the other, for example a short thin metallic wire immersed in a large quantity of water. If the quantity of water is large enough (or the wire small enough), then in the process of attaining thermal equilibrium the change in the physical state of the water will be entirely negligible compared with that of the wire. This situation is described differently according as we are primarily interested in the small system or in the large one.

If we are primarily interested in the small system, the wire, then we regard the water as a means of controlling the temperature of the wire and we refer to the water as a *temperature bath* or *thermostat*.

If on the other hand we are primarily interested in the large system, the water, we regard the wire as an instrument for recording the temperature of the water and we refer to the wire as a *thermometer*. This recording of temperature can be rendered quantitative by measuring some property of the thermometer, such as its electrical resistance, which varies with temperature.

§ 1. 10 TEMPERATURE SCALES

Since there is an infinite choice of kinds of thermometers so there is an infinite choice of empirical scales of temperature. We shall however see later that there is one particular scale of temperature which has outstandingly simple characteristics which can be described in a manner independent of the properties of any particular substance or class of substances. This scale is called the *absolute scale*. We shall later describe methods by which temperatures can be determined on the absolute scale. These methods, if they are to be precise, require elaborate apparatus and are extremely tedious. It is therefore general practice to use such a procedure to determine accurately a few standard temperatures on the absolute scale. Other subsidiary thermometers

of high sensitivity and convenient to use are calibrated at these standard temperatures according to the absolute scale. Intermediate temperatures are then measured by the subsidiary thermometers according to specified interpolation formulae between the standard temperatures. These interpolation formulae are so chosen that the temperatures recorded according to them are exactly the same as on the absolute scale at all the standard points and only differ very slightly, if at all, from the absolute scale at intermediate points. The unit of temperature is called a *degree*.

§ 1. 11 FIRST PRINCIPLE. ENERGY

We now formulate the *first principle* of thermodynamics.

The work required to bring a *thermally insulated* system from one completely specified state to a second completely specified state is independent of the source of the work and of the path through which the system passes from the initial to the final state.

It follows that when a system passes *adiabatically* from a state 1 to a state 2 the work w done on the system is given by

$$w = U(2) - U(1) \qquad \text{(adiabatic process)} \qquad 1.\,11.\,1$$

where $U(1)$, $U(2)$ depend only on the states 1, 2 respectively. In other words the work w done on the system is equal to the increase in the value of a function U of the state of the system. Using the symbol Δ to denote the increase in the value of a function, we can rewrite (1) as

$$w = \Delta U \qquad \text{(adiabatic process)} \qquad 1.\,11.\,2$$

where U is called the *energy* of the system. According to this property U is for a given system completely defined apart from an arbitrary additive constant, which is without physical significance since only changes of energy are measurable. The complete definition of U for each independent system thus requires an arbitrary conventional fixing of the state of zero energy. When this has been fixed, the energy in any other state is uniquely determined.

If the state of a system is defined by its temperature and certain other parameters such as composition and volume, and its temperature is changed while the other parameters are kept unchanged, then the change in the energy of the system may be referred to as a change in its *thermal energy*.

§ 1. 12 HEAT

The equality (1. 11. 2) holds only for an adiabatic process. In a process which is not adiabatic the system is said to *absorb a quantity of heat q*, or alternatively to *give off a quantity of heat* $-q$, where

$$q = \Delta U - w \qquad\qquad 1.\,12.\,1$$

This formula, which defines q, can be rewritten as

$$w + q = \Delta U \qquad\qquad 1.\,12.\,2$$

If we regard this as a statement of the *conservation of energy* and compare it with the corresponding statement for an adiabatic process, we observe that the energy of a system can be increased either by work done on it or by absorption of heat.

For an infinitesimal process equation (1) becomes

$$q = \mathrm{d}U - w \qquad\qquad 1.\,12.\,3$$

If of two systems in thermal contact the one *absorbs heat* and the other *gives off* this same quantity of *heat*, then we speak of a *flow of heat* from the second to the first. According to the zeroth principle such a *flow of heat* will take place only if the two systems are at different temperatures. We may thus regard *flow of heat* as a transfer of energy resulting from a temperature difference.

The extension of the mechanical principle of conservation of energy to include changes in thermal energy and the flow of heat was a gradual process, the earlier formulations being less rigorous than later ones. The principle is implied in a posthumous publication of Carnot (died 1832) and was placed on a firm experimental basis * by Joule (1840–45). More explicit statements of the principle were formulated by Helmholtz (1847) and by Clausius (1850). The formulation adopted here, which surpasses in rigour and clarity all earlier attempts, is due to Born † (1921).

§ 1. 13 CONVERSION OF WORK TO HEAT

The expression *conversion of work to heat* should be used with caution, since in general w and $-q$ are not numerically equal to each other. If however a system is taken through a complete cycle, then since its

---

* The reader interested in the history will find useful a critical summary with references to the original literature in Partington, *Chemical Thermodynamics* 1924 p. 11.

† Born, *Phys. Z.* 1921 **22** 218.

initial and final states are identical the initial and final values of U are the same and so

$$\Delta U = 0 \qquad w = -q \qquad \text{(complete cycle)} \qquad 1.13.1$$

We may then say that in the cycle the work w done on the system is converted into the balance of heat $-q$ given off by the system during the cycle, that is to say the excess of the heat given off over the heat absorbed in various parts of the cycle.

Again if a system is kept in a steady state while work is done on it, then, since its state remains unaltered, U does not change and so

$$\Delta U = 0 \qquad w = -q \qquad \text{(steady state)} \qquad 1.13.2$$

Here again we may say that in the steady state the work w done on the system is converted into the heat $-q$ given off by the system.

Except in the two special cases just mentioned, it is in general dangerous, if not meaningless, to speak of the conversion of work into heat or vice-versa. Unfortunately the expression is sometimes used incorrectly. Let us consider two simple practical examples which serve to illustrate the correct and incorrect use of the expression.

Consider as our system an ordinary *electric heater*, that is to say a resistor across which an electric potential difference E can be produced by closing a switch. Suppose that initially the resistor is in thermal equilibrium with its surroundings and the switch is open. When the switch is closed a current i flows through the resistor and the electrical work done on the heater in an element of time dt is

$$w = Ei\,dt \qquad 1.13.3$$

In the first instant this work produces an increase in the thermal energy of the resistor, so that

$$w = dU \qquad \text{(initially)} \qquad 1.13.4$$

But immediately the temperature of the resistor becomes higher than that of its surroundings and so there is a flow of heat $-q$ from the resistor to its surroundings. Thus in a time dt

$$w = dU - q \qquad \text{(generally)} \qquad 1.13.5$$

As the temperature difference between the resistance and its surroundings increases, so $-q/w$ increases towards the value unity.

Eventually a steady state is reached, the temperature of the resistor no longer increases and we have

$$w = -q \qquad dU = 0 \qquad \text{(steady state)} \qquad 1.\,13.\,6$$

Only when this steady state has been reached, and not until then, may one correctly speak of the conversion of the work w into the heat $-q$ in the time dt.

Now by way of contrast consider the system consisting of the electric heater together with a fluid surrounding it, the whole being thermally insulated. The work done on the system is still given by (3). But now since the whole system, consisting of resistor and fluid, is thermally insulated q is by definition zero, so that

$$w = dU \qquad q = 0 \qquad \text{(thermal insulation)} \qquad 1.\,13.\,7$$

We may now say that the work w is converted into *thermal energy*; to speak of its conversion to heat would be nonsense.

§ 1. 14 NATURAL, UNNATURAL AND REVERSIBLE PROCESSES

All the independent infinitesimal processes that might conceivably take place may be divided into three types: *natural processes, unnatural processes* and *reversible processes*. This classification is due to Planck [*].

Natural processes are all such as actually do occur in nature; they proceed in a direction towards equilibrium.

An *unnatural process* is one in a direction away from equilibrium; such a process never occurs in nature.

As a limiting case between natural and unnatural processes we have *reversible processes*, which consist of the passage in either direction through a continuous series of equilibrium states. Reversible processes do not actually occur in nature, but in whichever direction we contemplate a reversible process we can by a small change in the conditions produce a natural process differing as little as we choose from the reversible process contemplated.

We shall illustrate the three types by examples. Consider a system consisting of a liquid together with its vapour at a pressure P. Let the equilibrium vapour pressure of the liquid be p. Consider now the process of the evaporation of a small quantity of the liquid. If $P < p$, this is a natural process and will in fact take place. If on the other hand $P > p$, the process contemplated is unnatural and cannot take place; in fact the contrary process of condensation will take place. If $P = p$

[*] Planck, *Ann. Phys., Lpz.* 1887 **30** 563.

then the process contemplated and its converse are reversible, for by slightly decreasing or increasing P we can make either occur. The last case may be described in an alternative manner as follows. If $P = p - \delta$ where $\delta > 0$, then the process of evaporation is a natural one. Now suppose δ gradually decreased. In the limit $\delta \to 0$, the process becomes reversible.

§ 1. 15 REVERSIBLE PROCESS AND REVERSIBLE CHANGE

We have defined a *reversible process* as a hypothetical passage through equilibrium states. If we have a system interacting with its surroundings either through the performance of work or through the flow of heat, we shall use the term *reversible process* only if there is throughout the process equilibrium between the system and its surroundings. If we wish to refer to the hypothetical passage of the system through a sequence of internal equilibrium states, without necessarily being in equilibrium with its surroundings we shall refer to a *reversible change.* We shall illustrate this distinction by examples.

Consider a system consisting of a liquid and its vapour in mutual equilibrium in a cylinder closed by a piston opposed by a pressure equal to the equilibrium vapour pressure corresponding to the temperature of the system. Suppose now that there is a flow of heat through the walls of the cylinder, with a consequent evaporation of liquid and work done on the piston at constant temperature and pressure. The change in the system is a *reversible change*, but the whole process is a *reversible process* only if the medium surrounding the cylinder is at the same temperature as the liquid and vapour; otherwise the flow of heat through the walls of the cylinder is not reversible and so the process as a whole is not reversible, although the change in the system within the cylinder is reversible.

As a second example consider a flow of heat from one system in complete internal equilibrium to another system in complete internal equilibrium. Provided both systems remain in internal equilibrium then the change which each system undergoes is a *reversible change*, but the whole process of heat flow is not a *reversible process* unless the two systems are at the same temperature.

§ 1. 16 EQUILIBRIUM AND REVERSIBLE CHANGES

If a system is in complete equilibrium, any conceivable infinitesimal change in it must be reversible. For a natural process is an approach towards equilibrium, and as the system is already in equilibrium the

change cannot be a natural one. Nor can it be an unnatural one, for in that case the opposite infinitesimal change would be a natural one, and this would contradict the supposition that the system is already in equilibrium. The only remaining possibility is that, if the system is in complete equilibrium, any conceivable infinitesimal change must be reversible.

§ 1. 17 ENTROPY, ABSOLUTE TEMPERATURE AND SECOND PRINCIPLE

There exists a function S of the state of a system called the *entropy* of the system having the following properties.

The entropy of a system is the sum of the entropies of its parts. In this respect entropy is similar to mass, volume and energy. In other words entropy is an *extensive property* in the meaning to be defined in § 1. 23.

The entropy of a system can change in two distinct ways, namely by external changes and by internal changes. Symbolically we may write this as

$$dS = d_eS + d_iS \qquad\qquad 1.\,17.\,1$$

where dS denotes the increase of entropy of the system, d_eS denotes the part of this increase due to interaction with the surroundings and d_iS denotes the part of this increase due to changes taking place inside the system.

The entropy increase d_eS due to interaction with the surroundings is related to the heat q absorbed by the system from its surroundings by

$$d_eS = \frac{q}{T} \qquad\qquad 1.\,17.\,2$$

where T is a positive quantity depending only on the temperature of the system. We may therefore regard T as a particular scale of temperature and we call T the *absolute temperature*.

The entropy increase d_iS due to changes taking place inside the system is positive for all natural changes, is zero for all reversible changes and is never negative. In symbols

$$d_iS > 0 \qquad \text{(natural change)} \qquad 1.\,17.\,3$$

$$d_iS = 0 \qquad \text{(reversible change)} \qquad 1.\,17.\,4$$

Substituting (2) and (3) into (1), we obtain for a system at the absolute temperature T

$$dS > \frac{q}{T} \qquad \text{(natural change)} \qquad 1.17.5$$

If a system is not at a uniform temperature then we cannot apply (2) or (5) to the whole system, but we can do so to each part of the system which is at a uniform temperature.

Similarly substituting (2) and (4) into (1), we obtain

$$dS = \frac{q}{T} \qquad \text{(reversible change)} \qquad 1.17.6$$

These relations constitute the *second principle* of thermodynamics. It is to be noted that in this formulation the *absolute temperature* T and the *entropy* S are introduced simultaneously as two fundamental quantities. In a more mathematical formulation T^{-1} appears as an integrating factor leading to the complete differential dS.

The second principle was foreshadowed by the work of Carnot (1824). The first and second principles were coordinated by Clausius (1850) and by Kelvin (1851). *Absolute temperature* was introduced by Kelvin (1848). The conception of *entropy* was first used by Clausius in 1854 and the name also by Clausius in 1865.

According to the above relations S is indefinite to the extent of an arbitrary additive constant. This arbitrariness is however without physical significance, since only changes of entropy are observable or measureble. This indefiniteness can be removed by an arbitrary conventional fixing of a state of zero entropy for each independent system.

For a finite change, reversible throughout, equation (6) applies to each of the infinitesimal steps into which the finite change may be divided. Hence using Δ to denote the increase from the initial to the final value, we have

$$\Delta S = \Sigma \, \frac{q}{T} \qquad \text{(reversible change)} \qquad 1.17.7$$

where Σ denotes summation over all the steps.

In particular for a reversible cycle which leaves the system in a final state identical with the initial state

$$\Delta S == 0 \qquad \Sigma \, \frac{q}{T} = 0 \qquad \text{(reversible cycle)} \qquad 1.17.8$$

§ 1.18 KELVIN SCALE OF TEMPERATURE

It is obvious that the fundamental relation (1.17.2) used in defining entropy and absolute temperature would remain valid if the signs of

S and T were simultaneously reversed. We accordingly fixed the signs unambiguously by deciding that T shall be positive. The same relation (1. 17. 2) still remains valid if S is replaced by cS and T by $c^{-1}T$ where c is any positive number. Thus to complete the definitions of S and T we have to fix their scales, in other words to fix the unit of temperature called the *degree*. This is simply accomplished by assigning an arbitrary value to T at some specified temperature.

We define the temperature of the triple point of water, namely the only temperature at which ice, liquid water and water vapour are in mutual equilibrium, as exactly 273.16 degrees. The absolute scale of temperature with the size of the degree thus fixed is called the Kelvin scale, denoted by the symbol °K. Thus the triple point of water is by definition 273.16 °K.

§ 1. 19 CENTIGRADE DEGREE

We shall describe later in § 4. 13 how it is possible to measure the ratio of any two absolute temperatures, in particular the ratio of any absolute temperature to that of the triple point of water. Having assigned the value 273.16 °K to the triple point of water, it thus becomes possible to determine unambiguously any other temperature on the Kelvin scale. When the freezing point of water saturated with air at one atmosphere or the normal freezing point (n.f.p.) of water is so determined, it is found to be 273.150 °K. When the boiling point of pure water at one atmosphere or the normal boiling point (n.b.p.) of water is so determined, it is found to be 373.150 °K. Thus the n.b.p. of water exceeds the n.f.p. of water by just 100 degrees. This is of course no accident, but was the determining factor in the arbitrary choice of the size of the degree. Owing to this property of the chosen scale the degree is called a *centigrade degree*.

The present definition of the Kelvin scale of temperature received international recognition in 1954.* This definition implements a recommendation made by Kelvin † and revived by Giauque.‡ The procedure adopted previously of fixing the size of the degree by means of two temperatures (the n.f.p. and n.b.p. of water) is, as pointed out by Giauque, less direct, less reasonable and less convenient.

* *Comptes Rendus des Séances de la Dixième Conférence Générale des Poids et Mesures* 1954.
† Joule and Thomson, *Phil. Trans. Roy Soc.* 1854 **144** 351.
‡ Giauque, *Nature* 1939 **143** 623.

§ 1. 20 CELSIUS SCALE OF TEMPERATURE

For many practical purposes it is considered convenient to use a temperature scale such that the temperatures most usually met in the laboratory and in ordinary life shall be represented by numbers between 0 and 100. For this purpose the scale most used in scientific work is the *Celsius scale* (sometimes loosely called the *centrigrade scale*) and denoted by the letter C. The temperature on the Celsius scale is defined as the excess of the temperature on the Kelvin scale over that of the n.f.p. of water also on the Kelvin scale. Thus the relation between the two scales is

$$x \,°K = (x - 273.150) \,°C \qquad\qquad 1. 20. 1$$

$$y \,°C = (y + 273.150) \,°K \qquad\qquad 1. 20. 2$$

$$\text{n.f.p. of water} = 273.150 \,°K = 0 \,°C \qquad 1. 20. 3$$

$$\text{n.b.p. of water} = 373.150 \,°K = 100 \,°C \qquad 1. 20. 4$$

In both the *Kelvin scale* and the *Celsius scale* the unit is the *centigrade degree*, having the abbreviation deg. There are other scales based on other kinds of degrees, but these are little used in scientific work and need not be mentioned further.

§ 1. 21 HEAT FLOW AND TEMPERATURE

According to the zeroth principle of thermodynamics the condition for thermal equilibrium between two parts of a system is equality of temperature. We can now verify that this condition is consistent with the general condition of equilibrium, namely that any infinitesimal change should be reversible. We consider a thermally insulated system consisting of two parts α and β at uniform temperatures T^α and T^β respectively. The entropy S of the whole system is equal to the sum of S^α the entropy of α and S^β the entropy of β; that is to say

$$S = S^\alpha + S^\beta \qquad\qquad 1. 21. 1$$

Consider now the flow of an infinitesimal positive quantity q of heat from α to β. Then according to (1. 17. 2)

$$d_e S^\alpha = -\frac{q}{T^\alpha} \qquad\qquad 1. 21. 2$$

$$d_e S^\beta = \frac{q}{T^\beta} \qquad\qquad 1. 21. 3$$

The increase in the entropy of the whole system due to this flow of heat is therefore

$$\mathrm{d_e}S^\alpha + \mathrm{d_e}S^\beta = -\frac{q}{T^\alpha} + \frac{q}{T^\beta}$$

$$= q\left(\frac{1}{T^\beta} - \frac{1}{T^\alpha}\right) \qquad 1.\,21.\,4$$

The condition that the flow of positive heat q from α to β should be a natural process is that the consequent change of entropy of the whole system should be an increase, that is to say that the expression (4) should be positive. Thus heat will flow naturally from α to β provided

$$T^\alpha > T^\beta \qquad 1.\,21.\,5$$

We have thus reached the conclusion that according to our definition of the absolute temperature T, heat flows naturally from a higher to a lower absolute temperature.

If each of the phases α and β is in internal equilibrium then there are no changes of entropy other than that due to the flow of heat from α to β. If on the other hand, either phase, or both, is not in internal equilibrium there may be other entropy changes $\mathrm{d_i}S^\alpha$, $\mathrm{d_i}S^\beta$ superposed on that due to the flow of heat. These can only be positive, so that the increase in entropy of the whole system will then be greater than the expression (4). The above argument is not affected by such other natural processes proceeding as well as the flow of heat. This is an advantage of the particular formulation of the second principle which we have chosen *.

In the particular case that $T^\alpha = T^\beta$, the expression (4) vanishes; there is no entropy increase associated with the flow of heat. The two parts of the system are in thermal equilibrium and so the flow of heat contemplated is reversible.

§ 1. 22 PHASES

The simplest and most important kind of thermodynamic system may be considered as consisting of a finite number of homogeneous parts. As already mentioned in § 1. 03 each such homogeneous part is called a *phase*. Strictly, we should also include a finite number of

* Compare Prigogine and Defay, *Chemical Thermodynamics*, English translation by Everett, 1954 chap. 3.

inhomogeneous parts forming the boundaries between various pairs of homogeneous phases. However, for many purposes these inhomogeneous parts are of such small extent compared with the homogeneous parts that they may be ignored. We shall for the sake of simplicity so ignore them for the time being. At a later stage beginning at § 1. 51 we shall show how we may take account of them in an exact manner.

§ 1. 23 EXTENSIVE PROPERTIES

The mass of a system is clearly equal to the sum of the masses of its constituent phases. Any property, such as mass, whose value for the whole system is equal to the sum of its values for the separate phases is called an *extensive property* or a *capacity factor*.

Important examples of *extensive properties* are the energy U, the entropy S and the volume V. The energy U of a system is related to the energies U^a of the separate phases a by

$$U = \Sigma_a U^a \qquad\qquad 1.\,23.\,1$$

Similarly, for the entropy, we have

$$S = \Sigma_a S^a \qquad\qquad 1.\,23.\,2$$

and for the volume

$$V = \Sigma_a V^a \qquad\qquad 1.\,23.\,3$$

When we are considering a system of one phase only we may obviously omit the superscript a and shall usually do so.

§ 1. 24 INTENSIVE PROPERTIES

The density of a phase is clearly constant throughout the phase, because the phase is by definition homogeneous. Further, the density of a phase of a given kind and state is independent of the quantity of the phase. Any property of a phase with these characteristics is called an *intensive property* or an *intensity factor*.

The temperature T^a and the pressure P^a of a phase a are important examples of intensive properties.

§ 1. 25 PRESSURE OF PHASE

The fundamental property of the pressure is familiar from hydrostatics. It may be described by the statement that for any infinitesimal

increase dV^a of the volume of the phase a the work w^a done on the phase is given by

$$w^a = - P^a \, dV^a \qquad\qquad 1.\ 25.\ 1$$

where P^a is the pressure of the phase a.

§ 1. 26 CHEMICAL CONTENT OF PHASE

The content of a phase a is defined by the number n_i^a of units of quantity of each of a finite number of *independently variable chemical species* in the phase. The unit of quantity may be the gram, the pound or any other unit of mass. It need not necessarily be the same mass for different chemical species. In fact, it is usually most convenient to take as units of quantity the *mole*, that is a mass proportional to that given by the accepted chemical formula of the particular species. A purely thermodynamic definition of the mole will be given in § 4. 14. In anticipation of this we may use the mole as the unit of quantity for each chemical species and we shall so use it except where the contrary is stated.

§ 1. 27 CHEMICALLY INERT SPECIES

We must emphasise that in the previous section we specified that the chemical species by which the chemical content of the phase is described must be *independently variable*. In the absence of any chemical reactions there is no difficulty, but if some of the species can react chemically the recipe required for selecting a set of *independently variable* species is not so simple. In order to postpone this complication we shall exclude the possibility of chemical reactions until we come to § 1. 48 where we revert to the subject.

§ 1. 28 CLOSED AND OPEN PHASES

It will be convenient to refer to a phase of fixed content as *closed* and to one whose content can be varied by passage of substances to or from other phases as *open*. In a similar sense any part of a system may be referred to as *closed* or *open*.

§ 1. 29 DEGREES OF FREEDOM OF A CLOSED PHASE

Provided a closed phase is at rest and chemical reactions are excluded, the phase is always in internal equilibrium and so any infinitesimal change is reversible. An infinitesimal change can be irreversible

(natural) only if more than one phase or a chemical reaction is involved. Hence for a closed phase at rest, excluding chemical reactions, we have for any infinitesimal change

$$q = T\mathrm{d}S \qquad \text{(closed phase)} \qquad 1.\,29.\,1$$

$$w = -P\mathrm{d}V \qquad \text{(closed phase)} \qquad 1.\,29.\,2$$

while the first principle of thermodynamics gives for any infinitesimal process

$$\mathrm{d}U = q + w \qquad\qquad 1.\,29.\,3$$

Substituting from (1) and (2) into (3) we obtain

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V \qquad \text{(closed phase)} \qquad 1.\,29.\,4$$

As already made clear in § 1.03 a closed single phase has *two degrees of freedom*; that is to say two quantities must be fixed to complete the specification of its state. There is of course a wide possible choice of such pairs of independent variables. If one chooses the entropy S and the volume V as the two independent variables then equation (4) shows how the energy U depends on them. Such a choice of independent variables is not necessarily the most convenient. For example it might be preferable to choose the energy U and the volume V as the independent variables; the dependence on them of the entropy S is then obtained by simple transformation of (4) as

$$\mathrm{d}S = \frac{1}{T}\,\mathrm{d}U + \frac{P}{T}\,\mathrm{d}V \qquad \text{(closed phase)} \qquad 1.\,29.\,5$$

Other choices of independent variables will be discussed later.

§ 1. 30 CHEMICAL POTENTIALS

We can generalize formula (1. 29. 4) to an open phase or phase of variable content by writing formally

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \Sigma_i\,\mu_i\,\mathrm{d}n_i, \qquad 1.\,30.\,1$$

where Σ_i denotes summation over all the chemical species in the phase and μ_i is defined by

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,\,V,\,n_j} \qquad 1.\,30.\,2$$

n_j denoting all quantities like n_i except n_i itself.

The quantities μ_i were first introduced in this manner by Gibbs (1875), who called μ_i the *potential* [*] of the species i. It is more usual to call μ_i the *chemical potential* of i; sometimes μ_i is called the *partial potential* of i. All three names are unobjectionable.

The reader may well find the definition (2) of μ_i puzzling because a variation in the content of a phase keeping its entropy constant is an abstract idea not corresponding to any simple physical process. It must indeed be admitted that at this stage it is by no means clear to what extent equation (2) is a sufficient definition of μ_i. It should however be clear that there is nothing contradictory or inconsistent about equations (1) and (2). At the worst the definition of the μ_i's may be incomplete. We shall return to this point later in § 1. 36 and § 1. 47, meanwhile using (1) as a basis for development until we can obtain a simpler physical meaning of the chemical potentials μ_i.

The chemical potentials μ_i are intensive properties; that is to say that, like density, they have the same value in any phase as in a larger or smaller phase having the same temperature, pressure and relative composition. This may not be obvious at this stage but will become so later. Meanwhile this will be assumed.

§ 1. 31 CHARACTERISTIC FUNCTIONS

Formula (1. 30. 1) expresses the dependence of the energy U on the set of independent variables S, V, n_i. This set of independent variables is not by any means the most convenient. It is usually preferable to use T as an independent variable instead of S, and often preferable to use P as an independent variable instead of V. In order to change over to such alternative sets of variables, it is expedient to introduce certain new thermodynamic functions defined for each phase as follows.

$$F = U - TS \qquad\qquad 1.\,31.\,1$$

$$H = U + PV \qquad\qquad 1.\,31.\,2$$

$$G = U - TS + PV \qquad\qquad 1.\,31.\,3$$

If now we differentiate each of these and substitute for dU from (1. 30. 1) we obtain

$$dF = -\,SdT - PdV + \Sigma_i\,\mu_i\,dn_i \qquad\qquad 1.\,31.\,4$$

$$dH = \quad TdS + VdP + \Sigma_i\,\mu_i\,dn_i \qquad\qquad 1.\,31.\,5$$

$$dG = -\,SdT + VdP + \Sigma_i\,\mu_i\,dn_i \qquad\qquad 1.\,31.\,6$$

[*] Gibbs, *Collected Works* vol. 1 p. 65.

Since F, H, G like S, V, U are evidently extensive properties the F, H, G in a system of several phases are related to the F^a, H^a, G^a of the individual phases a by

$$F = \Sigma_a F^a \qquad\qquad\qquad 1.\,31.\,7$$

$$H = \Sigma_a H^a \qquad\qquad\qquad 1.\,31.\,8$$

$$G = \Sigma_a G^a \qquad\qquad\qquad 1.\,31.\,9$$

.It is clear that the dependence of F on the independent variables T, V, n_i is given simply and explicitly by (4). Similarly according to (5) and (6) H and G are simply expressed in terms of the independent variables S, P, n_i and T, P, n_i respectively. In view of these characteristics U is called a *characteristic function* for the variables S, V, n_i, and F is a *characteristic function* for the variables T, V, n_i; similarly H is a *characteristic function* for the variables S, P, n_i and G for the variables T, P, n_i.

The artifice of changing the independent variables by the introduction of the new functions defined by (1), (2) and (3) is an example of a Legendre transformation.*

The *characteristic functions* U, F, H, G are sufficient for all requirements. They are not however the only possible ones. For example by simple transformation of (1. 30. 1) we have

$$\mathrm{d}S = \frac{1}{T}\,\mathrm{d}U + \frac{P}{T}\,\mathrm{d}V - \frac{1}{T}\,\Sigma_i\,\mu_i\,\mathrm{d}n_i \qquad\qquad 1.\,31.\,10$$

showing that S is a *characteristic function* for the variables U, V, n_i. Again let us define two new quantities J and Y by

$$J = S - \frac{U}{T} = -\frac{F}{T} \qquad\qquad\qquad 1.\,31.\,11$$

$$Y = S - \frac{U}{T} - \frac{PV}{T} = -\frac{G}{T} \qquad\qquad 1.\,31.\,12$$

We now differentiate (11) and (12) and substitute for $\mathrm{d}S$ from (10), obtaining

$$\mathrm{d}J = \frac{U}{T^2}\,\mathrm{d}T + \frac{P}{T}\,\mathrm{d}V - \frac{1}{T}\,\Sigma_i\,\mu_i\,\mathrm{d}n_i \qquad\quad 1.\,31.\,13$$

$$\mathrm{d}Y = \frac{H}{T^2}\,\mathrm{d}T - \frac{V}{T}\,\mathrm{d}P - \frac{1}{T}\,\Sigma_i\,\mu_i\,\mathrm{d}n_i \qquad\quad 1.\,31.\,14$$

from which we see that J, like F, is a *characteristic function* for the variables T, V, n_i and Y, like G, is one for the variables T, P, n_i.

* Courant and Hilbert, *Methoden der Mathematische Physik* 1937 § 1. 6.

The functions J, Y have in recent times been largely superseded by F, G. In some applications the former have advantages over the latter, as will be seen later. In particular we shall see in chapter 2 that J, Y are more simply related to what is called statistical probability. We shall use mostly F, G but occasionally J, Y.

In a system of several phases a evidently

$$J = \Sigma_a J^a \qquad\qquad 1.\,31.\,15$$

$$Y = \Sigma_a Y^a \qquad\qquad 1.\,31.\,16$$

§ 1. 32 NAMES AND SYMBOLS FOR CHARACTERISTIC FUNCTIONS

Whereas the definition of the several thermodynamic functions is unambiguous and straightforward, there is unfortunately almost unbelievable absence of uniformity as to their names. We shall record briefly some of the alternative terminologies.

U, which we call *energy*, is sometimes called *total energy* and sometimes *internal energy*, the name used by Clausius.

H was called by Gibbs (1875) the *heat function for constant pressure*. It has the alternative names *heat function, total heat, heat content* and *enthalpy*, which is Greek for *heat content*. Of these we choose *heat function*. This name emphasizes that H, in contrast to q the heat absorbed, is a function of the state of the system.

The function F was called by Gibbs (1875) the *force function for constant temperature* * and by Helmholtz (1882) the *free energy* †. It has also been called the *work function* and the *Helmholtz free energy*. We shall use the alternative names *free energy* and *Helmholtz function*.

The function G is also due to Gibbs (1875). It is sometimes called the *total thermodynamic potential* and sometimes merely the *thermodynamic potential*. Unfortunately G has also been called *free energy*, thus causing confusion between F and G. To reduce such confusion G has sometimes been called the *Gibbs free energy*. We use the simpler name *Gibbs function*.

The functions J and Y were introduced by Massieu ‡ (1869) and the latter was widely used by Planck. We accordingly call J the *Massieu function* and Y the *Planck function*. It is interesting to note that these were the earliest characteristic functions, six years earlier than those introduced by Gibbs, namely F, G and H.

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* Gibbs, *Collected Works* vol. 1 p. 89.
† Helmholtz, *S. B. Preuss. Akad. Wiss.* 1882 1 22.
‡ Massieu, *C. R. Acad. Sci., Paris* 1869 69 858.

There has also been wide disparity between the notations of various authors. The table below gives a comparison of the choice of some of the best known authors.

Preferred Names	Entropy	Energy	Heat Function	Free Energy or Helmholtz Function	Gibbs Function	Massieu Function	Planck Function
Present Notation	S	U	H	F	G	J	Y
Massieu (1869)		U	U'			ψ	ψ'
Gibbs (1876)	η	ε	χ	ψ	ζ		
Helmholtz (1882)	S	U		F			
Duhem (1886)	S	U		F	φ		
Lorentz (1921, 1927)	η	ε		Ψ	ζ		
Planck (1932 edition)	S	U		F		Ψ	Φ
Lewis and Randall (1923)	S	E	H	A	F		
Partington (1924)	S	U	H	F	Z		
Schottky (1929)	S	U	H	F	G		
Fowler (1936)	S	E	H	F	G		
Brönsted (1936)	S	E	H	F	G		
De Donder and Van Rysselberghe (1936)	S	E	H	F	G		
Fowler and Guggenheim (1939)	S	E	H	F	G		
McDougall (1939)	S	E	H	A	F		
MacInnes (1939)	S	U	H	F	Z		
Slater (1939)	S	U	H	A	G		
Mayer and Mayer (1940)	S	E	H	A	F		
Zemansky (1943)	S	U	H	A	G		
Prigogine and Defay (1944)	S	E	H	F	G		
De Boer (1946)	S	U	W	F	G		
Everett (1954)	S	U	H	F	G		
Haase (1956)	S	U	H	F	G		
Münster (1956)	S	U	H	F	G		

Our notation has been chosen so as to agree with, or at least not to contradict, as many authors as possible especially those still alive, of whatever nationality *. In the use of S, U and F it conforms to the notation of Helmholtz (1882). It is unfortunate that pupils of the famous school in California founded by G. N. Lewis use F to denote

* This notation is recommended by the International Union of Pure and Applied Physics (1948, 1955) and by the International Union of Pure and Applied Chemistry (1947, 1955).

the *Gibbs function*, whereas some other American authors, as well as all Belgian, British, Danish, Dutch, French, German and Italian authors use F to denote the *Helmholtz function*. It is to be hoped that eventually international agreement will be reached.

§ 1. 33 FUNDAMENTAL EQUATIONS

Let us recollect four important relations from § 1. 30 and § 1. 31, namely

$$dU = \quad TdS - PdV + \Sigma_i \mu_i \, dn_i \qquad 1.33.1$$

$$dF = - SdT - PdV + \Sigma_i \mu_i \, dn_i \qquad 1.33.2$$

$$dH = \quad TdS + VdP + \Sigma_i \mu_i \, dn_i \qquad 1.33.3$$

$$dG = - SdT + VdP + \Sigma_i \mu_i \, dn_i \qquad 1.33.4$$

Each of these relates a *characteristic function* to its appropriate independent variables. Following Gibbs we call these *fundamental equations*. The relationship between the four *characteristic functions* U, H, F, G and the various pairs of independent variables chosen from the set S, T, V, P can be expressed schematically by

$$\begin{matrix} S & U & V \\ H & & F \\ P & G & T \end{matrix} \qquad 1.33.5$$

By means of a *fundamental equation* all the thermodynamic functions can be expressed in terms of the chosen characteristic function and its derivatives with respect to the corresponding independent variables.

For example choosing G (T, P, n_i) we obtain directly from (4)

$$S = - \frac{\partial G}{\partial T} \qquad 1.33.6$$

$$H = G - T \frac{\partial G}{\partial T} \qquad 1.33.7$$

$$V = \frac{\partial G}{\partial P} \qquad 1.33.8$$

$$F = G - P \frac{\partial G}{\partial P} \qquad 1.33.9$$

$$U = G - T \frac{\partial G}{\partial T} - P \frac{\partial G}{\partial P} \qquad 1.33.10$$

$$\mu_i = \frac{\partial G}{\partial n_i} \qquad 1.33.11$$

Similarly we could express all the thermodynamic functions in terms of U and its differential coefficients with respect to S, V, n_i, but not in terms of its differential coefficients with respect to T, V, n_i. This accounts for the untidiness produced by certain so-called elementary treatments wherein U, T, V, n_i are introduced as fundamental quantities without mentioning entropy until a late stage.

The set of fundamental equations (1) to (4) used by Gibbs has symmetry expressed by the scheme (5). It is the best known and most used set. It is however not always the most useful set. In some respects the set

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{1}{T} \Sigma_i \mu_i dn_i \qquad 1.\,33.\,12$$

$$dJ = \frac{U}{T^2} dT + \frac{P}{T} dV - \frac{1}{T} \Sigma_i \mu_i dn_i \qquad 1.\,33.\,13$$

$$dY = \frac{H}{T^2} dT - \frac{V}{T} dP - \frac{1}{T} \Sigma_i \mu_i dn_i \qquad 1.\,33.\,14$$

is more convenient. We recall that J is the *Massieu function* and Y the *Planck function*, defined respectively by

$$J = S - \frac{U}{T} = -\frac{F}{T} \qquad 1.\,33.\,15$$

$$Y = S - \frac{U}{T} - \frac{PV}{T} = -\frac{G}{T} \qquad 1.\,33.\,16$$

In particular we shall in chapter 2 find the fundamental equations (12) to (14) convenient in relating *classical thermodynamics* to *statistical thermodynamics*. For this purpose a fourth characteristic function is not needed.

§ 1. 34 DIMENSIONS AND UNITS

It is clear from the relations of § 1. 31 that U, H, F, G all have the same dimensions as energy and can be measured in joules or any other unit of energy. The products TS, PV and $\mu_i n_i$ also have the same dimensions as energy. Hence S has the same dimensions as energy/temperature and can be measured for example in J deg^{-1}. μ_i has the same dimensions as energy/mole and can be measured for example in J mole^{-1}.

Thermodynamic data are in fact often expressed in terms of a

different energy unit the *calorie* equal to 4.1840 J and referred to again in § 4. 06.

§ 1. 35 INTEGRATED RELATION

Any of the relations (1. 33. 1), (1. 33. 2), (1. 33. 3) or (1. 33. 4) can be integrated by the following artifice. Each of these relations holds for any variations of the independent variables. Let us now choose to keep T, P constant and make each n_i change by an increment proportional to itself. We accordingly put

$$\mathrm{d}T = 0 \qquad \mathrm{d}P = 0 \qquad \mathrm{d}n_i = n_i \, \mathrm{d}\xi \qquad 1.35.1$$

Physically this means that we increase the quantity of the phase in the proportion $(1 + \mathrm{d}\xi) : 1$ without altering its temperature, pressure or relative composition. Evidently then all other intensive properties, in particular the μ_i's, remain unaltered while all other extensive properties, in particular S, V, U, H, F, G, also increase in the proportion $(1 + \mathrm{d}\xi) : 1$. We have therefore

$$\mathrm{d}U = U\mathrm{d}\xi \qquad \mathrm{d}S = S\mathrm{d}\xi \qquad \mathrm{d}V = V\mathrm{d}\xi \qquad \mathrm{d}\mu_i = 0 \qquad 1.35.2$$

Substituting from (1) and (2) into (1. 33. 1) we obtain

$$U\mathrm{d}\xi = TS\mathrm{d}\xi - PV\mathrm{d}\xi + \Sigma_i \, \mu_i n_i \, \mathrm{d}\xi \qquad 1.35.3$$

Now integrating from $\xi = 0$ to $\xi = 1$, or alternatively dividing by $\mathrm{d}\xi$, we obtain

$$U = TS - PV + \Sigma_i \, \mu_i n_i \qquad 1.35.4$$

Alternatively we might substitute from (1) and (2) into (1. 33. 4), obtaining

$$G\mathrm{d}\xi = \Sigma_i \, \mu_i n_i \, \mathrm{d}\xi \qquad 1.35.5$$

Integrating from $\xi = 0$ to $\xi = 1$, or dividing by $\mathrm{d}\xi$, we obtain

$$G = \Sigma_i \, \mu_i n_i \qquad 1.35.6$$

which is equivalent to (4).

If instead we substituted into (1. 33. 2) or (1. 33. 3), we should again obtain the same result equivalent to (6).

We could also obtain the same result more directly by observing

that U is homogeneous and of first degree in the extensive properties S, V, n_i. Consequently by Euler's theorem

$$U = \frac{\partial U}{\partial S} S + \frac{\partial U}{\partial V} V + \Sigma_i \frac{\partial U}{\partial n_i} n_i$$

$$= TS - PV + \Sigma_i \mu_i n_i \qquad \qquad 1.\,35.\,7$$

the same as (4) and equivalent to (6).

§ 1.36 SINGLE COMPONENT PHASE

In a phase containing a single chemical substance we may omit the subscript $_i$. From each extensive property we derive an intensive property by dividing by the quantity of substance in the phase and we denote this intensive property by the subscript $_m$. Thus we write

$$V = nV_m \qquad \qquad 1.\,36.\,1$$

$$S = nS_m \qquad \qquad 1.\,36.\,2$$

$$U = nU_m \qquad \qquad 1.\,36.\,3$$

$$F = nF_m \qquad \qquad 1.\,36.\,4$$

$$H = nH_m \qquad \qquad 1.\,36.\,5$$

$$G = nG_m \qquad \qquad 1.\,36.\,6$$

If n is measured in moles then V_m is the volume per mole and is called *molar volume*. Analogous remarks apply to S_m, U_m, F_m, H_m and G_m.

For a phase consisting of a single chemical substance (1.35.6) reduces to

$$G = n\mu \qquad \qquad 1.\,36.\,7$$

Comparing (6) and (7) we obtain the striking relation

$$\mu = G_m \qquad \qquad 1.\,36.\,8$$

Thus for a single substance μ is the same as G per unit quantity e.g. per mole and there would be little point in using the distinct symbol μ if we were concerned only with single substances. But the relation (8) of course does not hold for mixtures and μ is then required. In other words μ is unnecessary in physics which is mainly concerned with single substances, but is important in chemistry which is concerned

with mixtures of and reactions between several substances. Hence the name *chemical potential*.

Suppose now that for a chemical species in its pure state, we conventionally assign an arbitrary value to U_m the energy per mole at some chosen value of the temperature, pressure and state of aggregation (e.g. crystal or liquid or gas). Suppose also we do the like for S_m the entropy per mole. Then subject to these arbitrary conventions, which are physically insignificant, U_m and S_m are completely defined at any other temperature and pressure and state of aggregation. Moreover T, P and V_m, the volume per mole, are unambiguously defined. Hence G_m is completely determined by

$$G_m = U_m - TS_m + PV_m \qquad\qquad 1.\,36.\,9$$

It follows according to (8), that having once chosen arbitrary zeros of U_m and S_m for a pure chemical substance μ is unambiguously defined.

This disposes of the question raised in § 1. 30 so far as pure chemical substances are concerned. The preciseness of definition of μ_i in a phase of several components will be examined in § 1. 47.

If now we apply the relation (1. 33. 4) to one mole of a single component, using (8) we obtain

$$d\mu = dG_m = -S_m\,dT + V_m\,dP \qquad\qquad 1.\,36.\,10$$

There is no term in dn, since n has the constant value unity. From (10) it follows immediately that

$$\frac{\partial \mu}{\partial T} = -S_m \qquad\qquad 1.\,36.\,11$$

$$\frac{\partial \mu}{\partial P} = V_m \qquad\qquad 1.\,36.\,12$$

By using the identity

$$\mu = G_m = H_m - 1 \qquad\qquad 1.\,36.\,13$$

we can transform (11) to

$$\mu - T\frac{\partial \mu}{\partial T} = H_m \qquad\qquad 1.\,36.\,14$$

or

$$\frac{\partial\,(\mu/T)}{\partial T} = -\frac{H_m}{T^2} \qquad\qquad 1.\,36.\,15$$

§ 1. 37 MOLE FRACTIONS

We are often interested only in the intensive properties of a phase and not at all in the amount of the phase. It is then convenient to describe the phase entirely by intensive variables. One such set of variables is T, P, x_i where x_i denotes the *mole fraction* defined by

$$x_i = \frac{n_i}{\Sigma_k n_k}. \qquad 1.37.1$$

where Σ_k denotes summation over all the species.

By definition the mole fractions satisfy the identity

$$\Sigma_i x_i = 1 \qquad 1.37.2$$

If the number of independent species or *components* is c, then of the $c + 2$ quantities T, P, x_i used to describe the state of the phase, apart from its amount, only $c + 1$ are independent owing to (2). We therefore say that a single phase of c components has $c + 1$ *degrees of freedom*.

§ 1. 38 GIBBS-DUHEM RELATION

We may, if we choose, describe the state of a single phase, apart from its size, by the set of intensive quantities T, P, μ_i. The number of these is $c + 2$. We have however seen that the number of degrees of freedom of a single phase is only $c + 1$. It follows that T, P, μ_i cannot be independently variable, but there must be some relation between them corresponding to the identity (1. 37. 2) between mole fractions. We shall now derive such a relation.

We differentiate (1. 35. 6) and obtain

$$dG = \Sigma_i \mu_i \, dn_i + \Sigma_i n_i \, d\mu_i \qquad 1.38.1$$

From (1) we subtract (1. 33. 4) and obtain

$$S dT - V dP + \Sigma_i n_i \, d\mu_i = 0 \qquad 1.38.2$$

Dividing (2) by $\Sigma_i n_i$ and denoting the average entropy per mole and the average volume per mole by S_m and V_m respectively, we find

$$S_m \, dT - V_m \, dP + \Sigma_i x_i \, d\mu_i = 0 \qquad 1.38.3$$

This is the sought relation between T, P and the μ_i's. Either (2) or (3)

is known as the Gibbs-Duhem relation *. It is particularly useful in its application to changes at constant temperature and pressure, when it may be written

$$\Sigma_i \, x_i \, D\mu_i = 0 \qquad (T, P \text{ constant}) \qquad 1.38.4$$

where we have used D to denote variations due to changes of composition at constant temperature and pressure. We shall frequently use this notation. In particular we shall return to these formulae in § 5.11.

§ 1.39 MULTIPHASE SYSTEMS

In the previous ten sections most of the formulae have been written explicitly for a single phase. Corresponding formulae for a system consisting of several phases are obtained by summation over all the phases. In particular from the fundamental equations in § 1.33 we obtain

$$dU = \quad \Sigma_a \, T^a \, dS^a - \Sigma_a \, P^a \, dV^a + \Sigma_a \, \Sigma_i \, \mu_i^a \, dn_i^a \qquad 1.39.1$$

$$dF = - \, \Sigma_a \, S^a \, dT^a - \Sigma_a \, P^a \, dV^a + \Sigma_a \, \Sigma_i \, \mu_i^a \, dn_i^a \qquad 1.39.2$$

$$dH = \quad \Sigma_a \, T^a \, dS^a + \Sigma_a \, V^a \, dP^a + \Sigma_a \, \Sigma_i \, \mu_i^a \, dn_i^a \qquad 1.39.3$$

$$dG = - \, \Sigma_a \, S^a \, dT^a + \Sigma_a \, V^a \, dP^a + \Sigma_a \, \Sigma_i \, \mu_i^a \, dn_i^a \qquad 1.39.4$$

where Σ_i denotes summation over the components and Σ_a denotes summation over the phases.

We are still postulating the absence of chemical reactions. This restriction will be removed in § 1.48.

§ 1.40 ADIABATIC CHANGES IN CLOSED SYSTEM

We recall that for any infinitesimal change in a closed system

$$dU = w + q \qquad 1.40.1$$

If the change is *adiabatic*, then by definition

$$q = 0 \qquad dU = w \qquad (\text{adiabatic}) \qquad 1.40.2$$

All conceivable infinitesimal adiabatic changes can moreover,

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* Gibbs, *Collected Works*, vol. 1 p. 88;
   Duhem, *Le Potentiel Thermodynamique et ses Applications* 1886 p. 33. The author has been unable to find any derivation of this relation by Duhem in any scientific journal. The derivation in the above mentioned text-book is the basis of that given here. The reference given by Hildebrand and Scott, *Solubility of Nonelectrolytes* 1950, is spurious.

according to the definitions in §1.15 and §1.17, be classified as follows:

$$dU = w \qquad dS > 0 \qquad \text{(natural adiabatic)} \qquad 1.40.3$$

$$dU = w \qquad dS = 0 \qquad \text{(reversible adiabatic)} \qquad 1.40.4$$

$$dU = w \qquad dS < 0 \qquad \text{(unnatural adiabatic)} \qquad 1.40.5$$

Suppose now that the whole system is enclosed by fixed rigid walls, so that $w = 0$. We then have the classification

$$dU = 0 \qquad dV = 0 \qquad dS > 0 \qquad \text{(natural adiabatic)} \qquad 1.40.6$$

$$dU = 0 \qquad dV = 0 \qquad dS = 0 \qquad \text{(reversible adiabatic)} \qquad 1.40.7$$

$$dU = 0 \qquad dV = 0 \qquad dS < 0 \qquad \text{(unnatural adiabatic)} \qquad 1.40.8$$

Suppose now, instead, that each phase a is partly bounded by a piston acting against a constant pressure P^a, so that

$$w = - \Sigma_a P^a \, dV^a = - \Sigma_a d \, (P^a V^a) = - d \, (\Sigma_a P^a V^a) \qquad 1.40.9$$

Then we have

$$dU = - d \, (\Sigma_a P^a V^a) \qquad 1.40.10$$

$$dH = d \, (U + \Sigma_a P^a V^a) = 0 \qquad 1.40.11$$

Consequently in this case we have the classification

$$dH = 0 \qquad dP^a = 0 \qquad dS > 0 \qquad \text{(natural adiabatic)} \qquad 1.40.12$$

$$dH = 0 \qquad dP^a = 0 \qquad dS = 0 \qquad \text{(reversible adiabatic)} \qquad 1.40.13$$

$$dH = 0 \qquad dP^a = 0 \qquad dS < 0 \qquad \text{(unnatural adiabatic)} \qquad 1.40.14$$

§ 1.41 ISOTHERMAL CHANGES IN CLOSED SYSTEM

Instead of a thermally insulated system, let us now consider a system whose temperature T is kept uniform and constant. This may be achieved by keeping the system in a temperature bath at the temperature T. Then according to the fundamental properties of entropy expounded in § 1.17 and in particular formulae (1.17.5) and (1.17.6) we have the classification of infinitesimal changes

$$dT = 0 \qquad d \, (TS) > q \qquad \text{(natural isothermal)} \qquad 1.41.1$$

$$dT = 0 \qquad d \, (TS) = q \qquad \text{(reversible isothermal)} \qquad 1.41.2$$

$$dT = 0 \qquad d \, (TS) < q \qquad \text{(unnatural isothermal)} \qquad 1.41.3$$

We also have according to the first principle of thermodynamics, in particular formula (1. 12. 3),

$$q = \mathrm{d}U - w = \mathrm{d}F + \mathrm{d}\,(TS) - w \qquad 1.\,41.\,4$$

using the definition (1. 31. 1) of F. Substituting from (4) into (1), (2) and (3) in turn we obtain

$$\mathrm{d}T = 0 \qquad w > \mathrm{d}F \qquad \text{(natural isothermal)} \qquad 1.\,41.\,5$$

$$\mathrm{d}T = 0 \qquad w = \mathrm{d}F \qquad \text{(reversible isothermal)} \qquad 1.\,41.\,6$$

$$\mathrm{d}T = 0 \qquad w < \mathrm{d}F \qquad \text{(unnatural isothermal)} \qquad 1.\,41.\,7$$

In particular if the system is enclosed by fixed rigid walls, so that $w = 0$, the classification becomes

$$\mathrm{d}T = 0 \qquad \mathrm{d}V = 0 \qquad \mathrm{d}F < 0 \qquad \text{(natural isothermal)} \qquad 1.\,41.\,8$$

$$\mathrm{d}T = 0 \qquad \mathrm{d}V = 0 \qquad \mathrm{d}F = 0 \qquad \text{(reversible isothermal)} \qquad 1.\,41.\,9$$

$$\mathrm{d}T = 0 \qquad \mathrm{d}V = 0 \qquad \mathrm{d}F > 0 \qquad \text{(unnatural isothermal)} \qquad 1.\,41.\,10$$

If on the other hand each phase a is partly bounded by a piston acting against a constant pressure P^a, then

$$w = -\,\Sigma_a\,P^a\,\mathrm{d}V^a = -\,\Sigma_a\,\mathrm{d}\,(P^a V^a) = -\,\mathrm{d}\,(\Sigma_a\,P^a V^a)$$
$$= \mathrm{d}\,(F - G) = \mathrm{d}F - \mathrm{d}G \qquad 1.\,41.\,11$$

from the definitions (1. 31. 1) and (1. 31. 3) of F and G respectively. Substituting from (11) into (5), (6) and (7) in turn, we obtain

$$\mathrm{d}T = 0 \qquad \mathrm{d}P^a = 0 \qquad \mathrm{d}G < 0 \qquad \text{(natural isothermal)} \qquad 1.\,41.\,12$$

$$\mathrm{d}T = 0 \qquad \mathrm{d}P^a = 0 \qquad \mathrm{d}G = 0 \qquad \text{(reversible isothermal)} \qquad 1.\,41.\,13$$

$$\mathrm{d}T = 0 \qquad \mathrm{d}P^a = 0 \qquad \mathrm{d}G > 0 \qquad \text{(unnatural isothermal)} \qquad 1.\,41.\,14$$

§ 1. 42 EQUILIBRIUM CONDITIONS. GENERAL FORM

We saw in § 1. 16 that if a system is in complete equilibrium then any conceivable change in it must be reversible. This enables us to put the conditions for equilibrium into various forms each of general validity.

If we first consider an infinitesimal change at constant volume, the system being thermally insulated, we have according to (1. 40. 7) the equilibrium conditions

$$\mathrm{d}S = 0 \qquad \mathrm{d}V = 0 \qquad \mathrm{d}U = 0 \qquad 1.\,42.\,1$$

If instead we consider an infinitesimal change keeping each phase a at constant pressure P^a, the whole system being thermally insulated, we have according to (1. 40. 13) the equilibrium conditions

$$dS = 0 \qquad dP^a = 0 \qquad dH = 0 \qquad 1.\,42.\,2$$

Thirdly let us consider an infinitesimal change at constant volume and constant uniform temperature (isothermal change). We now have according to (1. 41. 9) the equilibrium conditions

$$dT = 0 \qquad dV = 0 \qquad dF = 0 \qquad 1.\,42.\,3$$

Lastly by considering an infinitesimal change keeping each phase a at a constant pressure P^a and a constant uniform temperature T, we have according to (1. 41. 13) the equilibrium conditions

$$dT = 0 \qquad dP^a = 0 \qquad dG = 0 \qquad 1.\,42.\,4$$

Any one of the four sets of equilibrium conditions (1), (2), (3), (4) is sufficient by itself. They are all equivalent and each has an equal claim to be regarded as fundamental. It is curious that many text-books omit the second set (2). This omission disguises the symmetry between the several thermodynamic functions to which attention was drawn in § 1. 33.

§ 1. 43 CONDITIONS FOR STABILITY

In order to make clear what is meant by stability and instability in thermodynamic systems, we shall first discuss the significance of these expressions in a purely mechanical system. In fig. 1. 1 are shown in
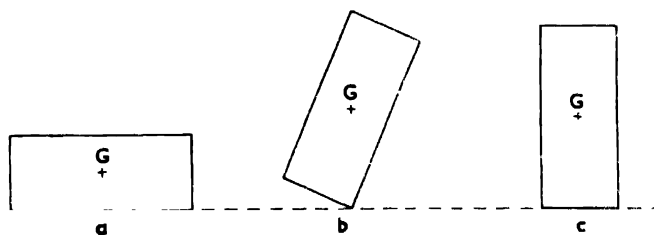
Fig. 1. 1. Stable and unstable equilibrium

section three different equilibrium positions of a box on a stand. In positions a and c the centre of gravity G is lower than in any infinitely

near position (consistent with the box resting on the stand); the gravitational potential energy is a minimum and the equilibrium is stable. If the position of the box be very slightly disturbed, it will of itself return to its former position. In position b, on the other hand, the centre of gravity G is higher than in any infinitely near position (consistent with the box resting on the stand), the gravitational potential energy is a maximum and the equilibrium is unstable. If the position of the box be very slightly disturbed, it will of itself move right away from its original position, and finally settle in some state of stable equilibrium such as a or c. As maxima and minima of the potential energy must alternate, so must positions of stable and of unstable equilibrium. Only stable equilibria are realizable in practice since the realization of an unstable equilibrium requires the complete absence of any possible disturbing factors.

Whereas positions a and c are both stable, one may describe a as *more stable* than c. Or one may say that a is *absolutely stable*, while c is *unstable compared to a*. By this is meant that in position c the potential energy is less than in any position differing only infinitesimally from c, but is greater than the potential energy in position a.

Similarly, the equilibrium of a thermodynamic system may be *absolutely stable*. On the other hand it may be stable compared with all states differing only infinitesimally from the given state, but unstable compared with some other state differing finitely from the given state; such states are called *metastable*. Truly *unstable* states analogous to b are unrealizable in thermodynamics, just as they are in mechanics.

The fact that all thermodynamic equilibria are stable or metastable, but never unstable, is equivalent to the fact that every natural process proceeds towards an equilibrium state, never away from it. Bearing this in mind and referring to the inequalities (1. 40. 6), (1. 40. 12), (1. 41. 8) and (1. 41. 12), we obtain the following alternative conditions for equilibrium

for given U and V that S is a *maximum*   1. 43. 1

for given H and P 's that S is a *maximum*   1. 43. 2

for given T and V that F is a *minimum* or that J is a *maximum*   1. 43. 3

for given T and P 's that G is a *minimum* or that Y is a *maximum* 1. 43. 4

Since $(\partial U/\partial S)_V = (\partial H/\partial S)_P = T > 0$, we may replace the first two conditions above by two others so as to obtain the more symmetrical set of equivalent conditions

for given S and V that U is a *minimum*   1. 43. 5

for given S and P 's that H is a *minimum*   1. 43. 6

for given T and V that F is a *minimum*   1. 43. 7

for given T and P 's that G is a *minimum*   1. 43. 8

Since T is a more convenient independent variable than S, the last two conditions are more useful, but nowise more fundamental, than the previous two.

Each of the above is the condition for stable equilibrium or for metastable equilibrium according as the minimum (or maximum) is absolute or only relative to immediately neighbouring states.

§ 1. 44 HYDROSTATIC EQUILIBRIUM

Consider a system of several phases in equilibrium at the temperature T. Suppose the phase a to increase in volume by an amount dV^a and the phase β to decrease by the same amount, the temperature and volume of the whole system and the composition of each phase remaining unchanged. Then, according to (1. 42. 3), the condition for equilibrium is

$$dF = dF^a + dF^\beta = 0 \qquad\qquad \text{1. 44. 1}$$

or by using (1. 39. 2)

$$- P^a \, dV^a + P^\beta \, dV^a = 0 \qquad\qquad \text{1. 44. 2}$$

and so

$$P^a = P^\beta \qquad\qquad \text{1. 44. 3}$$

That is to say that any two phases in hydrostatic equilibrium must be at the same pressure.

If we now consider two phases at the same temperature T and different pressures P^a and P^β, there will then not be hydrostatic equilibrium. There will be a tendency for the system to approach hydrostatic equilibrium by a change in which the volume of one phase, say a, increases by dV^a and that of the other phase β decreases by the same amount. Such a change is by definition a natural one. If we keep the temperatures of both phases constant, we therefore have, according to (1. 41. 8)

$$dF^a + dF^\beta < 0 \qquad\qquad \text{1. 44. 4}$$

or using (1. 39. 2)

$$- P^a \, dV^a + P^\beta \, dV^a < 0 \qquad\qquad \text{1. 44. 5}$$

If we suppose dV^α to be positive, it follows that

$$P^\alpha > P^\beta \qquad\qquad 1.\,44.\,6$$

That is to say, that the phase α with the greater pressure P^α will increase in volume at the expense of the phase β with the smaller pressure.

§ 1. 45 EQUILIBRIUM DISTRIBUTION BETWEEN PHASES

Consider a system of several phases, all at the same temperature T, but not necessarily at the same pressure. Suppose a small quantity dn_i^a of the species i to pass from the phase β to the phase a, the temperature of the whole system being kept constant. Then according to (1. 39. 2) we have

$$dF = - \Sigma_\gamma\, P^\gamma\, dV^\gamma + \mu_i^a\, dn_i^a - \mu_i^\beta\, dn_i^a \qquad 1.\,45.\,1$$

omitting the terms which obviously vanish. Since the total work w done on the whole system is $- \Sigma_\gamma\, P^\gamma\, dV^\gamma$, it follows from (1. 41. 5) that the process considered will be a natural one if

$$dF < - \Sigma_\gamma\, P^\gamma\, dV^\gamma \qquad \text{(natural process)} \qquad 1.\,45.\,2$$

Comparing (1) with (2) we obtain

$$(\mu_i^a - \mu_i^\beta)\, dn_i^a < 0 \qquad \text{(natural process)} \qquad 1.\,45.\,3$$

Thus dn_i^a in a natural process has the same sign as $\mu_i^\beta - \mu_i^a$. In other words each chemical species i tends to move from a phase where its potential μ_i is higher to another phase in which its potential is lower. Hence the name *potential* or *chemical potential* for μ_i.

If, instead of natural processes, we consider reversible processes we have equalities instead of inequalities; in particular instead of (3) we have

$$(\mu_i^a - \mu_i^\beta)\, dn_i^a = 0 \qquad \text{(reversible process)} \qquad 1.\,45.\,4$$

or

$$\mu_i^a = \mu_i^\beta \qquad \text{(equilibrium)} \qquad 1.\,45.\,5$$

We have obtained the important result that the condition for two phases to be in equilibrium with respect to any species is that the chemical potential of that species should have the same value in the two phases.

§ 1. 46 MEMBRANE EQUILIBRIUM

It is important to notice that, provided a system is at a uniform temperature, the condition for equilibrium between two phases of each chemical species is independent of that for other species and of that for hydrostatic equilibrium. If then two phases α and β are separated by a fixed wall permeable to some components i but not to other components j, the condition for the two phases to be in equilibrium as regards i is still

$$\mu_i^\alpha = \mu_i^\beta \qquad\qquad 1.\ 46.\ 1$$

but in this case in general

$$P^\alpha \neq P^\beta \qquad \mu_j^\alpha \neq \mu_j^\beta \qquad\qquad 1.\ 46.\ 2$$

Such a partial equilibrium is called a *membrane equilibrium*.

§ 1. 47 DEFINITENESS OF CHEMICAL POTENTIALS

In § 1. 30 we provisionally used Gibbs' definition of μ_i and pointed out the uncertainty at that stage whether that definition was sufficient. Later in § 1. 36 we showed that for a phase consisting of a single chemical substance μ is in fact, apart from trivial additive constants in U_m and S_m, completely defined by $\mu = G_m$. At last we are in a position to confirm that μ_i is likewise well defined in all phases.

We have merely to imagine the phase α in question separated from a phase β consisting of the pure substance i by a membrane permeable only to i. By adjustment of the pressure in the phase β it is in principle possible to achieve equilibrium with respect to i across the membrane. We then have

$$\mu_i^\alpha = \mu_i^\beta \qquad\qquad 1.\ 47.\ 1$$

and, since μ_i^β is adequately defined, we may regard (1) as a possible and sufficient definition of μ_i^α.

Incidentally the property of the μ_i's expressed by (1. 46. 1) or by (1) confirms that μ_i is, as hitherto assumed, an intensive property.

§ 1. 48 CHEMICAL REACTIONS. FROZEN EQUILIBRIUM

Hitherto we have explicitly excluded chemically reacting species from the system considered. We shall now explain how this restriction can be removed.

Owing to the slowness of attainment of some chemical equilibria, it can happen that the change towards chemical equilibrium is negli-

gible during a time sufficient for other kinds of equilibria to be observed and measured. In other cases the attainment of chemical equilibrium if not sufficiently slow for this to be the case can be made so by the addition to the system of a small quantity of a substance called an *anticatalyst* or merely by rigid exclusion of all traces of some other substance called a *catalyst*. Even in cases where the attainment of chemical equilibrium cannot be adequately slowed down in practice it is possible and legitimate to consider the hypothetical case wherein this has been achieved.

We are thus led to consider a system not in chemical equilibrium in which however the chemical reactions leading towards its attainment have been virtually suppressed. The system is then in a special kind of metastable equilibrium sometimes called *frozen equilibrium*. The several chemical species present are then virtually independent and so we can suppose a chemical potential μ assigned to each such species.

If we now suppose the addition of a suitable catalyst so as to *thaw* the *frozen equilibrium* then generally changes of composition will take place as a result of chemical reactions; such changes are of course natural processes. In the special case that the state of frozen equilibrium corresponds to complete chemical equilibrium, then no chemical change will take place on thawing. If we imagine a virtual chemical change to take place, such a change will then be a typical reversible change. If we write down the condition for this, we therefore obtain a relation between the μ's which is a condition of chemical equilibrium.

The final result may be described as follows. Instead of choosing a set of independent chemical species or *components*, we use the set of all the chemical species present whether independent or not and then obtain restrictive relations on their behaviour. The actual form of these restrictive relations will be obtained in the next section.

§ 1. 49 CHEMICAL EQUILIBRIUM

We consider a system of any number of phases maintained at a constant temperature T and constant pressure P. Then according to (1. 39. 4)

$$dG = \Sigma_a \Sigma_i \mu_i^a \, dn_i^a \qquad (T, P \text{ constant}) \qquad 1.\,49.\,1$$

where now, in contrast to previous practice, the species i are no longer all incapable of interacting chemically. According to (1. 41. 12) the condition for a natural process is

$$dG < 0 \qquad (T, P \text{ constant}) \qquad (\text{natural process}) \qquad 1.\,49.\,2$$

Combining (1) and (2) we obtain as the condition for a natural process

$$\Sigma_a \, \Sigma_i \, \mu_i^a \, dn_i^a < 0 \qquad \text{(natural process)} \qquad 1.\,49.\,3$$

Any chemical reaction at a given temperature and pressure can be described by a formula. As typical examples we quote

$$CaCO_3 \, (s) \rightarrow CaO \, (s) + CO_2 \, (g);$$
$$2NH_3 \, (g) \rightarrow N_2 \, (g) + 3H_2 \, (g);$$
$$\alpha\text{-glucose (aq)} \rightarrow \beta\text{-glucose (aq)};$$
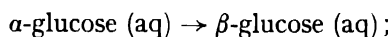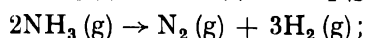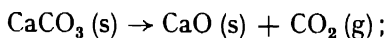
where (s) denotes a solid phase, (g) the gaseous phase and (aq) denotes an aqueous solution.

We can represent the most general chemical reaction symbolically by

$$\Sigma \, \nu_A \, A \rightarrow \Sigma \, \nu_B \, B \qquad\qquad 1.\,49.\,4$$

meaning that ν_A moles of A and the like react together to give ν_B moles of B and the like. The unit of quantity the *mole* is defined in such a way that the *stoichiometric numbers* ν can all be small integers. The symbols A and B are supposed to specify not only the kind of chemical species i but also in what phase it is present; in other words the label A implies the pair of labels i and a.

Now imagine the chemical process (4) to take place to the extent

$$\Sigma \, \nu_A \, d\xi \, A \rightarrow \Sigma \, \nu_B \, d\xi \, B \qquad\qquad 1.\,49.\,5$$

where $d\xi$ denotes a small number. Then the dn_i^a, corresponding to A is just $-\nu_A d\xi$. The inequality (3) thus becomes

$$\Sigma \, \nu_B \mu_B \, d\xi < \Sigma \, \nu_A \mu_A \, d\xi \qquad \text{(natural process)} \qquad 1.\,49.\,6$$

or if we assume $d\xi > 0$

$$\Sigma \, \nu_B \mu_B < \Sigma \, \nu_A \mu_A \qquad \text{(natural process)} \qquad 1.\,49.\,7$$

Thus the chemical reaction will in fact take place from left to right if the inequality (7) holds and conversely.

If we replace the inequalites by equalities we obtain as the condition for the chemical change in either direction to be a reversible process

$$\Sigma \, \nu_A \mu_A = \Sigma \, \nu_B \mu_B \qquad \text{(reversible process)} \qquad 1.\,49.\,8$$

In other words the condition for equilibrium with respect to the chemical process (5) is

$$\Sigma \, \nu_A \mu_A = \Sigma \, \nu_B \mu_B \qquad \text{(equilibrium)} \qquad 1.\,49.\,9$$

It is to be observed that the condition for equilibrium is obtained from the formula for the reaction by replacing the symbol for each species by that of the corresponding potential and replacing the sign $\rightarrow$ by $=$.

§ 1. 50 AFFINITY AND EXTENT OF REACTION

Let us consider a system consisting of any number of phases and chemical species all at the same temperature T. We need not however restrict ourselves to the usual case that all phases are at the same pressure, but may include membrane equilibria of the kind described in § 1. 46. Let us now consider the most general type of isothermal chemical or physico-chemical change which can conceivably take place in the system, denoting it symbolically as in the previous section by

$$\Sigma \, \nu_A \, A \rightarrow \Sigma \, \nu_B \, B \qquad\qquad 1.\,50.\,1$$

Two particularly simple examples of such changes are

(1) the passage of the substance i from phase a to phase β, provided of course that, if these two phases are separated by a membrane, this membrane is permeable to the species i;

(2) a homogeneous chemical reaction taking place in a single phase.

Any conceivable process can be regarded as a superposition of processes of types (1) and (2).

Let us now introduce a dimensionless quantity ξ, called the extent of reaction of the process, such that a change of ξ to $\xi + d\xi$ means that $\nu_A \, d\xi$ moles of A and the like react to form $\nu_B \, d\xi$ moles of B and the like. If now we suppose ξ to change to $\xi + d\xi$, we have according to (1. 39. 2)

$$dT = 0, \quad dF = -\, \Sigma_a \, P^a \, dV^a + (\Sigma \, \nu_B \mu_B - \Sigma \, \nu_A \mu_A) \, d\xi \qquad 1.\,50.\,2$$

while the work done on the system is

$$w = -\, \Sigma_a \, P^a \, dV^a \qquad\qquad 1.\,50.\,3$$

But we know from (1. 41. 5), (1. 41. 6) and (1. 41. 7) that the process considered is natural, reversible or unnatural according as w is greater than, equal to, or less than dF. Hence from (2) and (3) we obtain the conditions

$$(\Sigma \, \nu_B \mu_B - \Sigma \, \nu_A \mu_A) \, d\xi < 0 \qquad \text{(natural)} \qquad 1.\,50.\,4$$

$$(\Sigma \, \nu_B \mu_B - \Sigma \, \nu_A \mu_A) \, \mathrm{d}\xi = 0 \qquad \text{(reversible)} \qquad 1.\,50.\,5$$

$$(\Sigma \, \nu_B \mu_B - \Sigma \, \nu_A \mu_A) \, \mathrm{d}\xi > 0 \qquad \text{(unnatural)} \qquad 1.\,50.\,6$$

We now define a thermodynamic quantity A (not to be confused with the species A) by

$$A = \Sigma \, \nu_A \mu_A - \Sigma \, \nu_B \mu_B \qquad 1.\,50.\,7$$

and call A the *affinity* of the change (I). We can then rewrite (4), (5) and (6) as

$$A\,\mathrm{d}\xi > 0 \qquad \text{(natural)} \qquad 1.\,50.\,8$$

$$A\,\mathrm{d}\xi = 0 \qquad \text{(reversible)} \qquad 1.\,50.\,9$$

$$A\,\mathrm{d}\xi < 0 \qquad \text{(unnatural)} \qquad 1.\,50.\,10$$

We can express this result simply, as follows. Any chemical or physicochemical change will take place in the direction in which the *affinity* is positive. In the particular case that the *affinity* is zero, no change can take place in either direction and the system is in equilibrium with respect to the process considered.

The relation between the *affinity* A and the free energy F may be written symbolically

$$\mathrm{d}T = 0 \quad \mathrm{d}V = 0 \quad \mathrm{d}F = -A\,\mathrm{d}\xi \qquad 1.\,50.\,11$$

or alternatively

$$A = -\left(\frac{\partial F}{\partial \xi}\right)_{T,V} \qquad 1.\,50.\,12$$

provided it is understood that in varying F, not only are T and V kept constant, but no process takes place other than the one to which ξ refers. The affinity is likewise closely related to the other thermodynamic potentials U, H and G. In fact

$$A = -\left(\frac{\partial U}{\partial \xi}\right)_{S,V} = -\left(\frac{\partial H}{\partial \xi}\right)_{S,P} = -\left(\frac{\partial F}{\partial \xi}\right)_{T,V} = -\left(\frac{\partial G}{\partial \xi}\right)_{T,P}$$

$$= \Sigma \, \nu_A \mu_A - \Sigma \, \nu_B \mu_B \qquad 1.\,50.\,13$$

These definitions of *affinity* A and *extent of reaction* are essentially those introduced by De Donder * in 1922. This notation has not yet attained as wide a usage as it deserves. It is related to the better

* For detailed references see Prigogine and Defay, *Chemical Thermodynamics*, English translation by Everett 1954.

known notation due to G. N. Lewis as follows. In writing a chemical or physico-chemical process of the most general type as

$$\Sigma\, \nu_A\, A \to \Sigma\, \nu_B\, B \qquad\qquad 1.\,50.\,14$$

let us now agree that this shall imply

(1) constancy of T as previously;
(2) constancy of each P;
(3) increase of ξ by unity.

Let us further use the operator symbol Δ to denote the increase of any function of state when the change considered takes place. Subject to this interpretation of (14), we then have

$$A = -\,\Delta G = \Sigma\, \nu_A \mu_A - \Sigma\, \nu_B \mu_B \qquad\qquad 1.\,50.\,15$$

Thus at constant uniform temperature T and constant pressures P^α on the various phases, the affinity A for any change is equal to the decrease in the Gibbs function G and such a change will be a natural one if this affinity is positive.

§ 1. 51 SURFACE PHASES

We have hitherto assumed that every system consists of one or more completely homogeneous phases bounded by sharply defined geometrical surfaces. This is an over-simplification, for the interface between any two phases will rather be a thin layer across which the physical properties vary continuously from those of the interior of one phase to those of the interior of the other. We must now consider the thermodynamic properties of these surface layers between two phases. We shall begin by considering a plane interface and shall in § 1. 56 extend our considerations to curved interfaces.

The following treatment * is essentially that of van der Waals junior and Bakker. It is less abstract than the alternative treatment of Gibbs.

Fig. 1. 2 represents two homogeneous bulk phases, α and β, between which lies the surface layer σ. The boundary between σ and α is the plane AA′, that between σ and β the parallel plane BB′. All properties of σ are uniform in directions parallel to AA′, but not in the direction normal to AA′. At and near AA′ the properties are identical with

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* Van der Waals and Bakker, *Handb. Experimentalphysik* vol. **6** 1928.
See also Verschaffelt, *Bull. Acad. Belg. Cl. Sci.* 1936 **22** No. 4 pp. 373, 390, 402.
Guggenheim, *Trans. Faraday Soc.* 1940 **36** 398.

those of the phase α; at and near BB' they are identical with those of the phase β. Subject to these conditions there is freedom of choice in placing the planes AA' and BB'. It will be possible and natural,
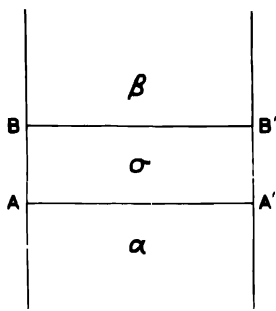
Fig 1. 2   Plane interface between two phases.

though not essential, so to place the planes AA' and BB' that the uniform distance between them is submicroscopic and usually less than 10^{-6} cm, if not less than 10^{-7} cm.

§ 1. 52 INTERFACIAL TENSION OF PLANE INTERFACE

Since the surface layer σ is a material system with a well defined volume and material content, its thermodynamic properties require no special definition. We may speak of its temperature, free energy, composition and so on just as for a homogeneous bulk phase. The only functions that call for special comment are the pressure and the interfacial tension. In any homogeneous bulk phase the force across any unit area is equal in all directions and is called the pressure. But in σ the force across unit area is not the same in all directions. If, however, we choose any plane of unit area parallel to AA' and BB', then the force across it has the same value for all positions of the plane whether it lie in α, β or σ; this value of the force across unit area is called the pressure P. Suppose, on the other hand, we choose a plane perpendicular to AA' and extending below AA' and above BB'; let this plane have the form of a rectangle of height h (parallel to AB) and of thickness l (perpendicular to the plane of the paper). Then the force across this plane will be equal to $Phl-\gamma l$, where P is the above-defined pressure and γ is called the *interfacial tension*. If the height of this plane is chosen to extend exactly from AA' to BB', then the force across it will be equal to $P\tau l-\gamma l$, if the height AB is denoted by τ. Let the surface layer have an area A and a volume V^σ so that

$$V^\sigma = \tau A \qquad\qquad 1. 52. 1$$

Suppose the area to be increased to $A + dA$, the thickness to $\tau + d\tau$ and the volume to $V^\sigma + dV^\sigma$, the material content remaining unaltered. Then the work done on σ by the forces across AA' and BB' is $-PAd\tau$. The work done by the forces parallel to the planes AA' and BB' is independent of the shape of the perimeter and for the sake of simplicity we may suppose the perimeter to be a rectangle. The work done by the latter forces is then evidently $-(P\tau-\gamma)\,dA$. The total work done on σ is therefore

$$-PAd\tau-(P\tau-\gamma)\,dA = -P\,(Ad\tau + \tau dA) + \gamma dA$$
$$= -PdV^\sigma + \gamma dA \qquad\qquad 1.52.\,2$$

This expression takes the place of $-PdV^\alpha$ for a homogeneous bulk phase.

§ 1. 53 FREE ENERGY OF SURFACE LAYER

For the most general variation of the free energy F^α of a homogeneous bulk phase we have the fundamental equation (1. 33. 2)

$$dF^\alpha = -S^\alpha\,dT - PdV^\alpha + \Sigma_i\,\mu_i\,dn_i^\alpha \qquad 1.53.1$$

For a surface phase σ the dependence of the free energy F^σ on the temperature and the composition will be exactly parallel to that for a bulk phase; this follows directly from the definitions of entropy and chemical potentials. But for the dependence of F^σ on size and shape we must replace $-PdV^\alpha$ by the expression (1. 52. 2). We thus obtain the formula

$$dF^\sigma = -S^\sigma\,dT - PdV^\sigma + \gamma dA + \Sigma_i\,\mu_i\,dn_i^\sigma \qquad 1.53.2$$

There is no need to add superscripts to T, P, μ_i, because these must have values uniform throughout α, β and σ in order that there may be thermal, hydrostatic and physico-chemical equilibrium.

§ 1. 54 INTEGRATED RELATION. GIBBS FUNCTION OF SURFACE PHASE

Formula (1. 53. 2) can be integrated by an artifice analogous to that used in § 1. 35 for integrating the fundamental equations of a bulk phase. We proceed as follows.

In formula (1. 53. 2) we now set

$$dT = 0 \quad dV^\sigma = -V^\sigma\,d\xi \quad dA = -Ad\xi \quad dn_i^\sigma = -n_i^\sigma\,d\xi \quad 1.54.1$$

and obtain

$$dF^\sigma = -d\xi\,(-PV^\sigma + \gamma A + \Sigma_i\,\mu_i n_i^\sigma) \qquad 1.54.2$$

This substitution corresponds physically to decreasing the extent of the surface layer σ by simply cutting off a portion at its edge, so that what remains is exactly like the original system except that it is reduced in extent in the ratio $(1 - d\xi) : 1$. It is therefore obvious that F^σ will also be reduced in the same ratio. It is also obvious that P, γ, μ_i remain unaltered. In mathematical terminology: at constant temperature and thickness F^σ is homogeneous of first degree in V^σ, A and n_i^σ and of zero degree in P, γ, μ_i. Thus the conditions (1) imply the simultaneous conditions

$$dF^\sigma = - F^\sigma \, d\xi \qquad dP = 0 \qquad d\gamma = 0 \qquad d\mu_i = 0 \qquad \text{1. 54. 3}$$

Substituting the value of dF^σ into (2) we obtain

$$- F^\sigma \, d\xi = - (- PV^\sigma + \gamma A + \Sigma_i \, \mu_i n_i) \, d\xi \qquad \text{1. 54. 4}$$

and equating coefficients of $d\xi$, or alternatively integrating from $\xi = 1$ to $\xi = 0$,

$$F^\sigma = - PV^\sigma + \gamma A + \Sigma_i \, \mu_i n_i^\sigma \qquad \text{1. 54. 5}$$

or

$$F^\sigma + PV^\sigma - \gamma A = \Sigma_i \, \mu_i n_i^\sigma \qquad \text{1. 54. 6}$$

Alternatively formula (6) can be derived mathematically from (1. 53. 2) by using Euler's theorem. Formula (6) is the analogue of

$$F^a + PV^a = \Sigma_i \, \mu_i n_i^a \qquad \text{1. 54. 7}$$

for a homogeneous bulk phase.

In analogy with the definition of the Gibbs function G^a of a bulk phase a

$$G^a = F^a + PV^a \qquad \text{1. 54. 8}$$

we now define the Gibbs function G^σ of the surface phase σ by

$$G^\sigma = F^\sigma + PV^\sigma - \gamma A \qquad \text{1. 54. 9}$$

We deduce from (1. 53. 2) and (9)

$$dG^\sigma = - S^\sigma \, dT + V^\sigma \, dP - A \, d\gamma + \Sigma_i \, \mu_i \, dn_i^\sigma \qquad \text{1. 54. 10}$$

$$G^\sigma = \Sigma_i \, \mu_i n_i^\sigma \qquad \text{1. 54. 11}$$

These two formulae are the analogues of the formulae

$$\mathrm{d}G^a = -S^a\,\mathrm{d}T + V^a\,\mathrm{d}P + \Sigma_i\,\mu_i\,\mathrm{d}n_i^a \qquad 1.\,54.\,12$$

$$G^a = \Sigma_i\,\mu_i n_i^a \qquad 1.\,54.\,13$$

for a homogeneous bulk phase.

§ 1. 55 ANALOGUE OF GIBBS-DUHEM RELATION

If we differentiate (1. 54. 6) we obtain

$$\mathrm{d}F^\sigma + P\mathrm{d}V^\sigma + V^\sigma\,\mathrm{d}P - \gamma\mathrm{d}A - A\mathrm{d}\gamma = \Sigma_i\,\mu_i\,\mathrm{d}n_i^\sigma + \Sigma_i\,n_i^\sigma\,\mathrm{d}\mu_i \qquad 1.\,55.\,1$$

If we now subtract (1) from (1. 53. 2) we obtain

$$S^\sigma\,\mathrm{d}T - V^\sigma\,\mathrm{d}P + A\mathrm{d}\gamma + \Sigma_i\,n_i^\sigma\,\mathrm{d}\mu_i = 0 \qquad 1.\,55.\,2$$

which is the analogue for a surface phase of the Gibbs-Duhem relation (1. 38. 2) for a bulk phase.

If we divide (2) throughout by A we obtain the more convenient form

$$S_u^\sigma\,\mathrm{d}T - \tau\mathrm{d}P + \mathrm{d}\gamma + \Sigma_i\,\Gamma_i\,\mathrm{d}\mu_i = 0 \qquad 1.\,55.\,3$$

where S_u^σ is the entropy per unit area and Γ_i the number of moles of the component i in unit area of the surface phase σ, defined respectively by

$$S_u^\sigma = S^\sigma/A \qquad 1.\,55.\,4$$

$$\Gamma_i = n_i^\sigma/A \qquad 1.\,55.\,5$$

We recall that τ is the thickness of the surface layer, that is to say the length AB in fig. 1.2.

§ 1. 56 INTERFACIAL TENSION OF CURVED INTERFACE

We must now consider under what conditions the formulae already derived for plane interfaces may be applied to curved interfaces. We shall see that the formulae strictly derived for plane interfaces may be applied to curved interfaces with an accuracy sufficient for experimental purposes provided that the thickness of the inhomogeneous surface layer is small compared with its radii of curvature [*].

For the sake of simplicity let us first consider a system consisting of two homogeneous bulk phases α and β connected by a surface layer σ having the form of a circular cylindrical shell. Fig. 1. 3 shows a cross-section of the phases α and β separated by the surface layer σ, bounded

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[*] Compare Guggenheim, *Trans. Faraday Soc.* 1940 **36** 408.

by the circular cylinders AA' and BB' with common axis O. There is complete homogeneity in the direction normal to the diagram. The properties of the surface layer σ are supposed identical at all points the same distance from the axis through O. Throughout the phase α and extending up to AA' there is a uniform pressure P^{α}; throughout the phase β, and extending down to BB', there is a uniform pressure P^{β}. Between AA' and BB' the pressure P_r parallel to the radii of the cylinders AA' and BB' varies continuously, but not necessarily monotonically, from the value P^{α} to the value P^{β}.
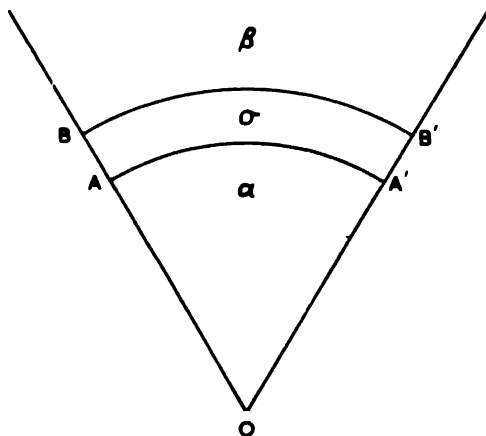
Fig 1 3. Curved interface between two phases.

In the previous discussion of plane surfaces it was pointed out that the geometrical planes AA' and BB' may be placed an arbitrary distance apart, provided that the inhomogeneous layer is contained between them. For the present discussion of curved surfaces it is on the contrary essential that the circular cylindrical surfaces AA' and BB' should be placed as near together as is consistent with the condition that the inhomogeneous layer be contained between them. According to this condition we may usually expect the distance AB to be about 10^{-7} cm or at most 10^{-6} cm. We shall denote by r distances measured radially from O, and in particular by r_{α} and r_{β}, the distances OA and OB respectively.

Whereas the force per unit area across any element of surface inside either homogeneous phase is independent of the orientation of the element (Pascal's law), this is not the case in the inhomogeneous layer σ. It is convenient to denote the force per unit area in the direction

parallel to the surface AA' and BB' by $P_r - Q$. Both P_r and Q are functions of r. Q is zero at $r = r_a$ and at $r = r_\beta$, but at least somewhere between Q is greater than zero. It is conceivable that Q might be negative somewhere between $r = r_a$ and $r = r_\beta$, but its average value in this range is unquestionably positive.

According to elementary statics the mechanical equilibrium of the matter enclosed by AA'B'B requires that for all values of r

$$d\,(P_r r) = (P_r - Q)\,dr \qquad 1.\,56.\,1$$

or

$$dP_r = -\,Q dr/r \qquad 1.\,56.\,2$$

If we integrate (2) from r_β to r_a, we obtain

$$P^a - P^\beta = \int_{r_a}^{r_\beta} \frac{Q}{r}\,dr \qquad 1.\,56.\,3$$

We now define quantities $\bar{r}$, γ, γ' by

$$2\bar{r} = r_a + r_\beta \qquad 1.\,56.\,4$$

$$\gamma = \int_{r_a}^{r_\beta} Q\,dr \qquad 1.\,56.\,5$$

$$\gamma' = \bar{r} \int_{r_a}^{r_\beta} \frac{Q}{r}\,dr \qquad 1.\,56.\,6$$

According to (6) we can rewrite (3) in the form

$$P^a - P^\beta = \gamma'/\bar{r} \qquad 1.\,56.\,7$$

If now the thickness of the interfacial layer is small compared with its curvature, that is to say

$$r_\beta - r_a \ll \bar{r} \qquad 1.\,56.\,8$$

then we may ignore any distinction between r_a, r_β, $\bar{r}$. We may then also ignore the distinction between γ and γ', and instead of (7) we may write

$$P^a - P^\beta = \gamma/\bar{r} \qquad 1.\,56.\,9$$

For the sake of simplicity we have confined ourselves to an interface in the form of a circular cylinder. For a spherical interface, we should have found by similar reasoning instead of (9),

$$P^a - P^\beta = 2\gamma/\bar{r} \qquad 1.\,56.\,10$$

For an interface of arbitrary shape the geometry is somewhat more complicated and the general formula obtained is

$$P^a - P^\beta = \gamma \left(\frac{1}{\varrho_1} + \frac{1}{\varrho_2} \right) \qquad 1.\,56.\,11$$

where ϱ_1, ϱ_2 are the principal radii of curvature of the interface.

Formula (11), like (9) and (10), implies ignoring the difference between lengths such as r_a, r_β. When the inequality (8) is not satisfied, the very idea of interfacial tension becomes ill-defined and probably useless.

Formula (11) is the basis, as we shall see, for the experimental determination of γ. The quantities measured are ϱ_1, ϱ_2 and $P^a - P^\beta$; then γ is calculated by means of (11). It follows that the very measurement of interfacial tension implies that the thickness of the interfacial layer be small compared with its radii of curvature.

§ 1. 57 DISCUSSION OF PRESSURE TERMS

Although the pressure difference $P^a - P^\beta$ is fundamental in the measurement of γ and so, one may say, in the definition of γ, we shall show that this pressure difference in certain other respects is insignificant for the properties of the interface. Let us again use τ to denote the thickness of the surface layer, so that

$$\tau = r_\beta - r_a \qquad 1.\,57.\,1$$

Our fundamental assumption for γ to be precisely defined may then be written

$$\frac{1}{\tau} \ggg \frac{1}{\varrho_1} + \frac{1}{\varrho_2} \qquad 1.\,57.\,2$$

Comparing (1. 56. 11) with (2) we see that

$$(P^a - P^\beta)\,\tau \lll \gamma \qquad 1.\,57.\,3$$

Now according to formula (1. 52. 2) the total work done on a plane surface layer when its volume and area are altered is

$$- P\mathrm{d}V^a + \gamma\mathrm{d}A \qquad 1.\,57.\,4$$

We cannot immediately apply this formula to a curved interface owing to the ambiguity in the meaning of P. Owing however to the inequality (3) we may expect and can in fact verify that in practice

$$|\,(P^a - P^\beta)\,\mathrm{d}V^a\,| \ll |\,\gamma\mathrm{d}A\,| \qquad 1.\,57.\,5$$

Consequently formula (4) is sufficiently accurate if P denotes either P^α or P^β or any intermediate pressure.

To recapitulate, for an interface whose thickness is small compared with its curvature, and it is only for such interfaces that the interfacial tension is defined, we may apply unchanged the fundamental formulae obtained for plane interfaces in §§ 1. 51—1. 55.

§ 1. 58 PRESSURE WITHIN A BUBBLE

Let us consider a bubble having the form of a thin spherical film of liquid of internal and external radii r_1 and r_e. If P^1 denotes the pressure nearer to the centre than the film, P^e the pressure further from the centre than the film, and P' the pressure in the liquid film itself, we have, according to (1. 56. 10)

$$P^1 - P' = \frac{2}{r_1} \gamma \qquad\qquad 1.\,58.\,1$$

$$P' - P^e = \frac{2}{r_e} \gamma \qquad\qquad 1.\,58.\,2$$

so that

$$P^1 - P^e = \left(\frac{2}{r_1} + \frac{2}{r_e}\right) \gamma \qquad\qquad 1.\,58.\,3$$

or, neglecting the difference between r_1 and r_e

$$P^1 - P^e = \frac{4}{r} \gamma \qquad\qquad 1.\,58.\,4$$

§ 1. 59 DETERMINATION OF INTERFACIAL TENSION

The commonest method of determining the value of the interfacial tension γ depends on formula (1. 56. 11). This method is shown diagrammatically in fig. 1. 4. Two fluid phases α and β are represented, the one shaded the other not shaded. They are separated partly by the plane surfaces AA'' and A'A''', and partly by the curved surface BB' in the capillary tube PP'Q'Q of internal radius r. We may, with sufficient accuracy, regard the surface BB' as a segment of a sphere. Let the centre of this sphere be O and let θ be the angle between OB and the horizontal OX or alternatively the angle between the tangential plane to BB' at B and the wall of the vertical capillary tube. Then the radius of curvature of the surface BB' is $r/\cos\theta$.

Let P^0 denote the pressure at the plane surfaces AA'' and A'A'''.

It will also be the pressure inside the capillary tube at the height AA'. Let the pressures at the height BB' be denoted by P^α in the phase α and by P^β in the phase β. Then
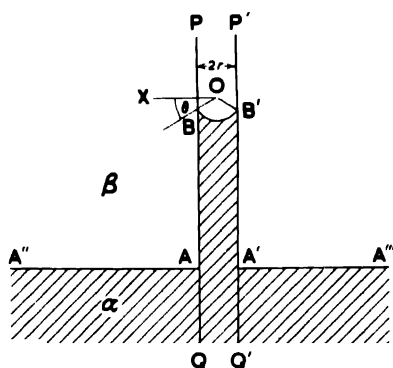
Fig. 1 4. Capillary rise due to interfacial tension.

$$P^\alpha = P^0 - \varrho^\alpha gh \qquad\qquad 1.\,59.\,1$$

$$P^\beta = P^0 - \varrho^\beta gh \qquad\qquad 1.\,59.\,2$$

where ϱ^α, ϱ^β denote the densities of the phases α and β, g is the acceleration due to gravity, and h is the height AB. But, according to (1. 56. 10)

$$P^\beta \cdot P^\alpha = 2\,\frac{\cos\theta}{\sim}\,\gamma \qquad\qquad 1.\,59.\,3$$

Comparing (1), (2) and (3), we obtain

$$\frac{\cos\theta}{\sim}\,\gamma = (\varrho^\alpha - \varrho^\beta)\,gh \qquad\qquad 1.\,59.\,4$$

Thus, from measurement of ϱ^α, ϱ^β, r, θ and h, we can calculate γ. In the special case that a is a liquid and β the vapour phase in equilibrium with it, it will usually be allowable to neglect ϱ^β compared with ϱ^α so that (4) reduces to

$$2\,\frac{\cos\theta}{\sim}\,\gamma \quad \varrho^\alpha gh \qquad\qquad 1.\,59.\,5$$

In the case that the surface BB' is concave towards the bottom, its radius of curvature will have the opposite sign, and so h will also have the opposite sign. That is to say, BB' will lie below AA'.

§ 1. 60 INDEPENDENCE OF INTERFACIAL TENSION OF CURVATURE

Let us now turn to the question whether the interfacial tension depends on the curvatures. We shall see that when the question is precisely defined it answers itself. In asking the question it is not sufficient to state that we vary the curvatures; we require also to state what we keep constant. For the question to be useful it should apply to the actual conditions of the experimental measurement of interfacial tension. For definiteness let us consider the capillary rise method described in the preceding section. The values of the temperature T and the chemical potentials μ are uniform throughout the system, and so, whatever be the size and shape of the capillary, these variables have the same values at the curved surface where the surface tension is measured, as in the bulk phases. Hence to be useful the question should be worded: how does γ depend on ϱ_1, ϱ_2 for given values of T and the μ's? According to equation (1. 55. 3) the variation of γ under these restrictions is given by

$$d\gamma = \tau dP \qquad\qquad 1.\ 60.\ 1$$

In its present application the ambiguity in the exact meaning of P does not matter, since we have already verified that $(P^{\alpha} - P^{\beta})\,\tau$ is negligible. If now we consider a curved interface, say in a capillary, in equilibrium with a plane interface and we integrate (1) from the pressure at the plane surface to the pressure at the curved interface (either side of it) we again find that the integral of the right side is always negligible. Consequently γ has effectively the same value for the curved surface as for the plane surface with which it is in equilibrium. This is a statement of a principle usually assumed whenever an interfacial tension is measured. It is experimentally verified by the fact that within the experimental accuracy the same value is found for the interfacial tension when capillaries of different size are used, but this verification can be realized only for capillaries with diameters considerably greater than the lower bound allowed by the theory.

§ 1. 61 GIBBS' TREATMENT OF CURVED INTERFACES

The problem of curved interfaces was treated by Gibbs in a manner which appears to be quite different and more rigid. The essence of Gibbs' treatment is that he replaced the term

$$\gamma dA \qquad\qquad 1.\ 61.\ 1$$

for a plane interface by terms of the form

$$\gamma dA + C_1 d\left(\frac{1}{\varrho_1}\right) + C_2 d\left(\frac{1}{\varrho_2}\right) \qquad 1.\ 61.\ 2$$

and assumed implicitly that, provided the radii of curvature are not too small, one may assign to C_1 and C_2 the values appropriate to a plane surface. It is then obvious from symmetry that $C_1 = C_2$, and so (2) can be written in the simpler form

$$\gamma dA + Cd\left(\frac{1}{\varrho_1} + \frac{1}{\varrho_2}\right) \qquad 1.\ 61.\ 3$$

where C is independent of ϱ_1, ϱ_2. So far so good. Gibbs then set out to prove that his geometrical surface could be so placed that C vanishes. The reasoning adduced is far from simple, and Gibbs' meaning is not even always clear. It seems that Gibbs was himself aware of the difficulty of being precise in this particular piece of reasoning. He discussed the variation of a plane interface by bending it and used the sentence * "also at and about the surface let the state of the matter *so far as possible be the same* as at and about the plane surface in the initial state of the system". The words written in italics are in their vagueness unlike Gibbs' usual style. The whole treatment of Gibbs, like the treatment in this book, postulates complete equilibrium throughout the entire system. It is therefore impossible to conceive of a variation of an interface apart from a variation in at least one of the bulk phases. It is clear that Gibbs realized this difficulty and tried to overcome it by flexible wording.

Gibbs then claimed to show that the position required for his geometrical surface to make C vanish would be either inside the non-homogeneous layer or at most at a distance from it comparable to the thickness of the layer. He here used the words "on account of the thinness of the nonhomogeneous film", and it seems clear that this *thinness* is an essential assumption common to Gibbs' treatment and that outlined above. If then the assumption $\tau \ll \varrho$ is essential, it is more convenient and simpler to introduce it at the outset and so considerably simplify the whole argument.

§ 1. 62 BASIS OF THERMODYNAMIC PRINCIPLES

The *zeroth principle* in § 1. 08, the *first principle* in § 1. 11 and the *second principle* in § 1. 17 have all been quoted as fundamentally

* Gibbs, *Collected Works* vol. 1 p 226.

independent assumptions. From this point of view their justification is the empirical fact that all conclusions from these assumptions are without exception in agreement with the experimentally observed behaviour in nature.

The form in which these principles have been enunciated is essentially that used by Born *. There are otner alternative forms some more, others less abstract, but all of an entirely empirical nature; that is to say that their justification is agreement between their implications on the one hand and experiment on the other.

It is, however, possible to obtain a deeper insight into the fundamental principles from a statistical point of view. It is in fact possible to derive these principles from our knowledge of the structure of matter including the elements of quantum theory together with a single statistical assumption of a very general form. It is a matter of taste whether to choose as a basis several empirical principles which make reference neither to atomic theory nor to quantum theory, or to choose a single principle superposed on atomic theory and quantum theory. The former choice, the one adopted in this book, is the method of *classical thermodynamics*; the latter choice corresponds to the more modern science which we call *statistical thermodynamics*.

There are however other relations of a general nature which follow naturally and directly from the statistical thermodynamic formulation, but which cannot be derived from the zeroth, first and second principles of classical thermodynamics. The relations to which we refer are of several types concerning respectively

(a) entropy changes in highly disperse systems (i.e. gases);
(b) entropy changes in very cold systems (i.e. when $T \to 0$);
(c) entropy changes associated with mixing of very similar substances (e.g. isotopes).

The three types are of comparable importance. They resemble one another in relating to entropy changes. Their formulation in terms of classical thermodynamics is either complicated or inaccurate or else involves reference to conceptions inherently foreign to classical thermodynamics. As already mentioned they all follow naturally and directly from the statistical thermodynamic formulation.

We shall devote the following chapter to a digression on *statistical thermodynamics*, describing in very general terms the methods of this science just sufficiently to give the reader an idea of the source of the

* Born, *Phys. Z* 1921 **22** 218.

relations in question without attempting to derive them in detail. The reader interested in the complete derivations must refer to a standard text-book on *statistical thermodynamics*.

§ 1. 63 THIRD PRINCIPLE

It has been customary to refer to the three types of general relations mentioned in the preceding section in three quite different ways. The relations of type (*a*) are referred to as the determination of *entropy constants*, those of type (*b*) as the *third law* of thermodynamics and those of type (*c*) merely as the formulae for *entropy of mixing*. This biased discrimination between types of relations of comparable importance and generality is difficult to defend. We accordingly reject this unbalanced terminology and instead choose as our *third principle* the following statement.

By the standard methods of *statistical thermodynamics* it is possible to derive for certain entropy changes general formulae which cannot be derived from the *zeroth, first* or *second principles of classical thermo-dynamics*. In particular one can obtain formulae for entropy changes in highly disperse systems (i.e. gases), for those in very cold systems (i.e. when $T \to 0$) and for those associated with the mixing of very similar substances (e.g. isotopes).

CHAPTER 2

DIGRESSION ON STATISTICAL
THERMODYNAMICS

§ 2. 01 MICRODESCRIPTIONS AND MACRODESCRIPTIONS OF A SYSTEM

According to quantum theory the state of a system is completely specified by its eigenfunction. To each state there corresponds one eigenfunction and to each eigenfunction one state. The expression *degenerate state of weight Ω* is an abbreviation for a group of states between which we do not care to distinguish. Such a description of the system we shall call a *microdescription*.

It is often though not always, possible to regard the system as consisting of a large number of almost independent *units* (molecules, atoms, ions, electrons) and to express each eigenfunction of the system as a linear combination of products of the eigenfunctions of all the units. According to the *symmetry restrictions*, if any, imposed on the eigenfunctions of the system, we then obtain three alternative sets of statistical formulae referred to by the names of Fermi-Dirac, Bose-Einstein and Boltzmann, respectively. These three alternatives, however, arise only when we express the eigenfunctions of the system in terms of those of the constituent units. As long as we refer only to the eigenfunctions of the whole system, we shall not need to consider these three alternatives separately. Nor shall we do so until we reach § 2. 10.

When we describe the equilibrium properties of a system by thermodynamic methods, we are not interested in such a precise description as the *microdescription*, but are content with a more crude large scale description, which we shall call a *macrodescription*. For example a possible *macrodescription* of the system would be a precise statement of the energy, the volume, the exact chemical composition (and in special cases other quantities all measurable on a large scale) of each homogeneous part or phase. For brevity we shall confine our discussion initially to systems whose macrodescription requires a precise statement of only four quantities. The extension of the argument to more complicated systems should be obvious. Initially we shall take the

first of these quantities to be the energy, the second to be the volume, the third to be the empirical composition; the nature of the fourth quantity is best indicated by some specific examples.

Example 1. Let us consider a definite quantity of hydrogen (free from deuterium) of given energy and given volume. Then we can complete the description by a statement of what fraction of it is *para*, the remaining fraction being *ortho*.

Example 2. If instead of hydrogen, we have lactic acid we can complete the description by a statement of what fraction is *dextro*, the remaining fraction being *laevo*.

Example 3. If the system consists of a given quantity of iodine of given energy and volume we can complete the description by a statement of what fraction is in the *diatomic* form I_2, the remainder being in the *monatomic* form I.

Example 4. If the system consists of a given quantity of tin of given energy and volume, we can complete the description by stating what fraction is *white*, the remainder being *grey*.

Example 5. If the system consists of a given quantity of carbon dioxide, we may complete the description by stating what fraction is *liquid*, the remainder being *vapour*.

In the first three examples it is assumed either that the system is homogeneous or, if it consists of two phases, that we are not interested in the relative amounts, these being determined by the other conditions. Another example that might be suggested is a system of a given quantity of hydrogen of given energy and volume for which we were interested both in the ratio of *para* to *ortho* and in the ratio of *liquid* to *vapour*. Such a system, however, requires five quantities, instead of four, to complete its macrodescription and so lies outside the class which we shall discuss, although the extension of the treatment to such a system in fact offers no difficulty.

Having made clear by these examples the nature of the fourth independent variable describing the system we shall denote this variable by ξ. It corresponds closely to the quantity ξ which, following De Donder, we introduced in § 1.50 and which we call the extent of reaction of a physico-chemical change. It is not a necessary property of ξ that one should be able completely to control its value, provided that its value can in principle be measured by *macroexperiments*.

§ 2. 02 SYSTEM OF GIVEN ENERGY, VOLUME AND COMPOSITION

Let us now consider in more detail a system of prescribed energy U, prescribed volume V and containing a prescribed number N of atoms or molecules of a given kind. Let the number of independent eigenfunctions of the system consistent with the prescribed values of U, V, N and corresponding to a particular value of the parameter ξ be denoted by $\Omega(\xi)$. As long as we are not interested in distinguishing between the states of equal ξ, we may group them together into a degenerate state of weight $\Omega(\xi)$.

Then the *fundamental assumption of statistical thermodynamics* is the following.

The average properties of the system for prescribed values of U, V, N can be derived statistically by averaging over all degenerate states of given ξ, assigning to each a weight $\Omega(\xi)$.

In other words it is assumed that for given U, V, N the *probability* of a particular value of ξ is

$$\frac{\Omega(\xi)}{\Sigma_\xi \, \Omega(\xi)} \qquad\qquad 2.\ 02.\ 1$$

It is customary to refer to the numerator $\Omega(\xi)$ in (1) as the *thermodynamic probability* of the particular value of ξ. It must be emphasized that a *thermodynamic probability* thus defined is not a *probability* in the usual sense of the word. Whereas an ordinary *probability* such as (1) is a number less than or equal to unity, the *thermodynamic probability* is generally a large number.

For reasons which will appear later $\Omega(\xi)$ had better be called the *thermodynamic probability of ξ for given U, V, N* than merely the thermodynamic probability of ξ. Another name for $\Omega(\xi)$ is the *partition function for given U, V, N, ξ*. The reason for this name will also become clearer as we proceed.

We now define a quantity $S(U, V, N, \xi)$ by the relation

$$S(U, V, N, \xi) = k \ln \Omega(\xi) \qquad\qquad 2.\ 02.\ 2$$

where k is a universal arbitrary constant whose value will be settled later. It can then be shown as we shall see later that in a macroscopic system S has all the properties of the entropy of the system in the macrostate defined by U, V, N, ξ. Formula (2) is a precise formulation of the well-known relation due to Boltzmann to whom the name *thermodynamic probability* is due.

We shall see that Boltzmann's relation (2) between the *entropy* and

the *thermodynamic probability* or *partition function* for given U, V, N, ξ is merely one of a number of relations of a similar type between a *characteristic function* for a particular set of variables on the one hand and the *thermodynamic probability* or *partition function* for the same set of variables on the other.

§ 2. 03 CHARACTERISTIC OF MACROSCOPIC SYSTEM

According to the *fundamental assumption* of *statistical thermodynamics* in a system of given U, V, N the average value ξ_{Av} of ξ is determined by

$$\xi_{Av} = \frac{\Sigma_\xi \, \xi \, \Omega \, (\xi)}{\Sigma_\xi \, \Omega \, (\xi)} \qquad 2.\ 03.\ 1$$

and the average value of ξ^2 by

$$(\xi^2)_{Av} = \frac{\Sigma_\xi \, \xi^2 \, \Omega \, (\xi)}{\Sigma_\xi \, \Omega \, (\xi)} \qquad 2.\ 03.\ 2$$

Thus in general $(\xi_{Av})^2$ is not the same as $(\xi^2)_{Av}$.

In other words there are fluctuations measured by

$$[(\xi - \xi_{Av})^2]_{Av} = (\xi^2)_{Av} - (\xi_{Av})^2$$

$$= \frac{\Sigma_\xi \, \Omega \, (\xi) \, \Sigma_\xi \, \xi^2 \, \Omega \, (\xi) - \Sigma_\xi \, \xi \, \Omega \, (\xi) \, \Sigma_\xi \, \xi \, \Omega \, (\xi)}{\Sigma_\xi \, \Omega \, (\xi) \, \Sigma_\xi \, \Omega \, (\xi)} \qquad 2.\ 03.\ 3$$

It can be shown generally that the larger the system the less important is this fluctuation and that for any macroscopic system the fluctuation is entirely trivial compared with $(\xi_{Av})^2$ itself. Without attempting a proof we shall consider a little more closely how this comes about.

There is some value ξ_m of ξ for which $\Omega(\xi)$ has a maximum. Generally speaking the larger the system the sharper is this maximum and for any macroscopic system it is very sharp indeed. On each side of this maximum term $\Omega(\xi_m)$ there will be many terms almost as great as $\Omega(\xi_m)$. Then there will be a still greater number of terms appreciably smaller but not negligible; but an overwhelming majority of the terms will be entirely negligible, and this majority includes all those terms in which ξ differs appreciably from ξ_m.

As a result of such considerations it can be shown that whereas the average properties are strictly determined by attributing to each ξ the weight $\Omega(\xi)$, in any macroscopic system we may with trivial inaccuracy ignore all values of ξ other than the value ξ_m at which $\Omega(\xi)$ is maximum.

Thus for any macroscopic system we have with trivial inaccuracy

$$\xi_{Av} = \xi_m \qquad\qquad 2.\,03.\,4$$

$$(\xi^2)_{Av} = \xi_m^2 \qquad\qquad 2.\,03.\,5$$

and so on.

It is instructive to relate this important characteristic of a macroscopic system to the quantity $S\,(U, V, N, \xi)$ defined by (2. 02. 2), namely

$$S\,(U, V, N, \xi) = k \ln \Omega\,(\xi) \qquad\qquad 2.\,03.\,6$$

Let us now define another quantity $S\,(U, V, N)$ by

$$S\,(U, V, N) = k \ln \Sigma_\xi \, \Omega\,(\xi) \qquad\qquad 2.\,03.\,7$$

Then by definition it is evident that

$$S\,(U, V, N) > S\,(U, V, N, \xi) \qquad \text{(all values of } \xi) \qquad 2.\,03.\,8$$

Let us now consider the ratio

$$\frac{\ln \Sigma_\xi\, \Omega\,(\xi) - \ln \Omega\,(\xi_m)}{\ln \Omega\,(\xi_m)}. \qquad\qquad 2.\,03.\,9$$

It can be shown that roughly speaking $\Omega\,(\xi_m)$ is of the order $N!$ and $\Sigma_\xi\, \Omega\,(\xi)/\Omega\,(\xi_m)$ is of the order N^a where a is comparable with unity. Hence the numerator in (9) is of the order $a \ln N$ and the denominator of the order $N \ln N$. Thus the expression (9) is of the order a/N or near enough N^{-1}, which is entirely negligible in any macroscopic system. Hence, although the inequality (8) is strictly true by definition for all values of ξ, in any macroscopic system when ξ has the special value ξ_m we may with trivial inaccuracy replace the inequality (8) by the equality

$$S\,(U, V, N) = S\,(U, V, N, \xi_m) \qquad\qquad 2.\,03.\,10$$

We shall see in § 2. 05 that the functions denoted by S have in fact the properties of entropy. Anticipating this identification let us call $S\,(U, V, N, \xi)$ the *entropy for fixed* ξ and $S\,(U, V, N)$ the *entropy for equilibrium* ξ.

Consider now a system of given U, V, N with ξ *frozen*. Now suppose that by introduction of a catalyst ξ is *thawed*, so that it takes its equilibrium value. By definition the entropy changes from $S\,(U, V, N, \xi)$ to $S\,(U, V, N)$ and also by definition this is always an increase. Only in the special case that the initial value of ξ was ξ_m, the entropy increase from $S\,(U, V, N, \xi_m)$ to $S\,(U, V, N)$ for any macroscopic

system is trivial. In other words although $S(U, V, N)$ the entropy for *equilibrium* ξ is by definition greater than the entropy for ξ *fixed at its equilibrium value* ξ_m, the difference is in a macroscopic system negligible and trivial.

We shall see later that a macroscopic system has other characteristics similar and parallel to that just formulated. These characteristics can be summed up in the single sentence that in a *macroscopic* system *fluctuations* of measurable properties are *negligible*.

§ 2. 04 SYSTEM OF GIVEN TEMPERATURE, VOLUME AND COMPOSITION

We shall now consider a system whose volume V and composition N are still prescribed, but instead of prescribing the energy we shall suppose the system to be immersed in a large temperature bath with which it can exchange energy so that the energy of the system can now take various values U_0, U_1, and so on. Let us now enumerate the eigenfunctions of the system for the prescribed values of V and N and for some definite value of ξ; let there be Ω_r such eigenfunctions corresponding to an energy $U_r(V, N, \xi)$.

From the *fundamental assumption of statistical thermodynamics*, as stated in § 2. 01, without any further assumptions it can be shown that the average properties of the system in the temperature bath for the prescribed values of V and N can be derived statistically by averaging over all degenerate states attaching to each state r of specified ξ and U_r a weight

$$\Omega_r \, e^{-\beta U_r} \qquad\qquad 2.\,04.\,1$$

where β is determined entirely by the temperature bath and so may be regarded as a temperature scale.

The fact that the parameter β is found to appear without any new assumption is the statistical thermodynamic basis of the *zeroth principle of classical thermodynamics*. The *statistical thermodynamic* equivalent of the *first principle of classical thermodynamics* is merely the principle of *conservation of energy* applied on the microscopic scale, that is to say applied to molecules, atoms, electrons, etc. Thus this principle is from the point of view of statistical thermodynamics not a new law but merely one item in general atomic quantum theory.

To relate the *second principle of classical thermodynamics* to *statistical thermodynamics* we make certain algebraic transformations. We begin by defining a function $J(\beta, V, N, \xi)$ by

$$J(\beta, V, N, \xi) = k \ln \{\textstyle\sum_r \Omega_r(\xi)\, e^{-\beta U_r}\} \qquad\qquad 2.\,04.\,2$$

where the summation is over all states of given ξ and k is a universal arbitrary constant.

In the system with temperature specified by β there will be fluctuations of U, but the experimentally measurable U will be U_{Av} the average value of U. Let us now consider the value of U_{Av} for specified β, V, N and ξ. Using the weighting factors (1) we have

$$U_{Av}(\beta, V, N, \xi) = \frac{\Sigma_r U_r \Omega_r(\xi) e^{-\beta U_r}}{\Sigma_r \Omega_r(\xi) e^{-\beta U_r}}$$

$$= -\frac{\partial}{\partial \beta} \ln \{\Sigma_r \Omega_r(\xi) e^{-\beta U_r}\} = -\frac{1}{k} \frac{\partial}{\partial \beta} J(\beta, V, N, \xi) \qquad 2.04.3$$

using (2).

Again associated with the fluctuations in U there will be fluctuations in the pressure $-(\partial U/\partial V)$, but the experimentally measured pressure P will be $-(\partial U/\partial V)_{Av}$, where the subscript $_{Av}$ denotes averaging with the weight factor (1). We accordingly have for given β, V, N and ξ

$$P = -\left(\frac{\partial U}{\partial V}\right)_{Av} = \frac{-\Sigma_r \frac{\partial U_r}{\partial V} \Omega_r(\xi) e^{-\beta U_r}}{\Sigma_r \Omega_r(\xi) e^{-\beta U_r}}$$

$$= \frac{1}{\beta} \frac{\partial}{\partial V} \ln \{\Sigma_r \Omega_r(\xi) e^{-\beta U_r}\} = \frac{1}{k\beta} \frac{\partial}{\partial V} J(\beta, V, N, \xi) \qquad 2.04.4$$

using (2).

Let us now make the further algebraic substitution

$$k\beta = T^{-1} \qquad 2.04.5$$

and use T as an independent variable instead of β. We now have in place of (3) and (4)

$$U_{Av}(T, V, N, \xi) = -\frac{\partial}{\partial (T^{-1})} J(T, V, N, \xi)$$

$$= T^2 \frac{\partial}{\partial T} J(T, V, N, \xi) \qquad 2.04.6$$

$$P = T \frac{\partial}{\partial V} J(T, V, N, \xi) \qquad 2.04.7$$

Combining (6) with (7) we have

$$dJ = \frac{U_{Av}}{T^2} dT + \frac{P}{T} dV \qquad \text{(given } N, \xi) \qquad 2.04.8$$

Comparing (8) with (1. 31. 13) we see that the dependence of J defined by (2) on T defined by (5) and on P is precisely the same as the dependence of the *Massieu function* on the absolute temperature and on the pressure. It can in fact be shown that T defined by (5) has all the properties of absolute temperature and J defined by (2) has all the properties of the *Massieu function*. This constitutes a brief summary of how the *second principle of classical thermodynamics* follows as a natural deduction from *statistical thermodynamics*.

For the benefit of the reader not familiar with the *Massieu function J*, we recall that it is related to the *free energy* or *Helmholtz function F* by

$$J = -F/T \qquad\qquad 2.\,04.\,9$$

and that either J or F is a characteristic function for the independent variables T, V, N.

We can now substitute from (5) into (1) and so have as a weighting factor for each state r

$$\Omega_r\, e^{-U_r/kT} \qquad\qquad 2.\,04.\,10$$

and this factor is called *Boltzmann's factor*. From (10) it is clear that kT has the dimensions of energy. k is a universal constant called *Boltzmann's constant*. If we use the *Kelvin scale* of temperature with the *centigrade degree* then

$$k = 1.380_3 \times 10^{-16}\ \text{erg deg}^{-1} \qquad\qquad 2.\,04.\,11$$

From (10) we see that the average properties of the system for prescribed values of T, V, N and unspecified ξ can be obtained by averaging over all ξ attaching to each ξ a weight $Q\,(T, \xi)$ defined by

$$Q\,(T, \xi) = \Sigma_r\, \Omega_r\,(\xi)\, e^{-U_r/kT} \qquad\qquad 2.\,04.\,12$$

The function $Q\,(T, \xi)$ is usually called the *partition function*, but a more precise name is the *partition function for given T, V, N, ξ*. An alternative name is the *thermodynamic probability for given T, V, N, ξ*.

Substituting from (5) and (12) into (2) we obtain

$$J\,(T, V, N, \xi) = k \ln Q\,(T, \xi) \qquad\qquad 2.\,04.\,13$$

We observe that this relation between the *characteristic function J* and the statistical probability $Q\,(T, \xi)$ for given T, V, N, ξ is completely analogous to *Boltzmann's relation* (2. 02. 2) between the characteristic function S and the thermodynamic probability $\Omega(\xi)$ for given U, V, N, ξ.

§ 2. 05 FURTHER CHARACTERISTICS OF MACROSCOPIC SYSTEM

Let us consider the individual terms of $Q\,(T,\,\xi)$ defined by (2. 04.12). Let us denote the maximum term by

$$\Omega_m\,e^{-U_m/kT}, \qquad\qquad 2.\,05.\,1$$

noting that this Ω_m is not the same as the $\Omega\,(\xi_m)$ of § 2. 03. Generally speaking the larger the system the sharper this maximum and for any macroscopic system it is so sharp that all terms in $Q\,(T,\,\xi)$ in which U_r differs appreciably from U_m are entirely trivial. Moreover, although the actual number of terms $Q\,(T,\,\xi)$ comparable with (1) may be great, the ratio

$$\frac{\ln Q\,(T,\,\xi)-\ln\,(\Omega_m\,e^{-U_m/kT})}{\ln\,(\Omega_m\,e^{-U_m/kT})} \qquad\qquad 2.\,05.\,2$$

is roughly of the order a/N where a is far nearer to unity than to N. Hence in any macroscopic system the ratio (2) is effectively zero and we may therefore replace the definition (2. 04. 2) of J by

$$J = k\ln\,(\Omega_m\,e^{-U_m/kT}) \qquad\qquad 2.\,05.\,3$$

It follows again that with an inaccuracy trivial for a macroscopic system

$$U_{Av} = T^2\,\frac{\partial J}{\partial T} = U_m \qquad\qquad 2.\,05.\,4$$

From the classical definition (1. 31. 11) or (1. 33. 15) of the *Massieu function J*, we have

$$S = J + \frac{U}{T} \qquad\qquad 2.\,05.\,5$$

We accordingly in *statistical thermodynamics* define a function $S\,(T,\,V,\,N,\,\xi)$ by

$$S\,(T,\,V,\,N,\,\xi) = J\,(T,\,V,\,N,\,\xi) + \frac{U_{Av}}{T} \qquad\qquad 2.\,05.\,6$$

Using (3), (4) and (5) we obtain from (6)

$$S\,(T,\,V,\,N,\,\xi) = k\ln\Omega_m\,(\xi) \qquad\qquad 2.\,05.\,7$$

Now comparing (7) with (2.02. 2) we obtain the striking result

$$S\,(T,\,V,\,N,\,\xi) = S\,(U_{Av},\,V,\,N,\,\xi) \qquad\qquad 2.\,05.\,8$$

Thus although the definition of entropy at a specified temperature by means of (6) together with (2. 04. 13) is entirely different from the definition of entropy at a specified energy by means of (2. 02. 2), yet for a macroscopic system the difference between the two is quite trivial.

This characteristic property of a macroscopic system may be described in the following instructive but less exact way. If we define S by

$$S = k \ln \Omega \, (\xi) \qquad\qquad 2.\,05.\,9$$

then in a system of specified energy Ω must denote the number of states having *precisely* this energy, whereas in a system of specified temperature Ω denotes the number of states of energy *nearly* equal to the average energy. The question immediately arises how nearly. The answer is that for a *macroscopic system* it just does not make any difference.

§ 2. 06 SYSTEM OF GIVEN TEMPERATURE, PRESSURE AND COMPOSITION

We now consider a system of prescribed composition surrounded by a temperature bath and enclosed by a piston subjected to a prescribed pressure P. We construct the double sum

$$W \, (T, P, N, \xi) = \Sigma_r \, \Sigma_s \, \Omega_{rs} \, (\xi) \; e^{-U_r/kT} \; e^{-PV_s/kT} \qquad 2.\,06.\,1$$

where the summation extends over all energies U_r and all volumes V_s consistent with the prescribed value of ξ. It can then be shown without any new assumptions that we can correctly derive the average (equilibrium) properties of the system for the prescribed values of T, P, N by averaging over all values of ξ attaching to each a weight $W \, (T, P, N, \xi)$.

We call $W \, (T, P, N, \xi)$ the *thermodynamic probability for given T, P, N, ξ* or the *partition function for given T, P, N, ξ*. It is related to the *Planck function Y*, which is a characteristic function for the independent variables T, P, N, ξ, by

$$Y \, (T, P, N, \xi) = k \ln W \, (T, P, N, \xi) \qquad\qquad 2.\,06.\,2$$

analogous to (2. 02. 2) and (2. 04. 13).

For the benefit of the reader unfamilar with the *Planck function Y* we recall its relation to the *Gibbs function G*, namely

$$Y = - G/T \qquad\qquad 2.\,06.\,3$$

Provided the system is macroscopic we may again with only trivial inaccuracy replace W by its maximum term, say

$$\Omega_m\,(\xi)\;e^{-U_m/kT}\;e^{-PV_m/kT} \qquad 2.\,06.\,4$$

so that we may replace (2) by

$$Y\,(T,\,P,\,N,\,\xi) = k\ln\Omega_m\,(\xi) - \frac{U_m}{T} - \frac{PV_m}{T} \qquad 2.\,06.\,5$$

From (1) and (5) we immediately verify that

$$(U + PV)_{Av} = T^2\frac{\partial \text{\textit{Y}}}{\partial T} = U_m + PV_m \qquad 2.\,06.\,6$$

$$V_{Av} = -\,T\,\frac{\partial Y}{\partial P} = V_m \qquad 2.\,06.\,7$$

as we should expect according to (1. 31. 14). Furthermore comparing (5) with (1. 33. 16) we obtain

$$S\,(T,\,P,\,N,\,\xi) = k\ln\Omega_m\,(\xi) \qquad 2.\,06.\,8$$

verifying that for a macroscopic system the entropy at given T, P is indistinguishable from the entropy at given $U = U_m$ and $V = V_m$.

§ 2. 07 SYSTEM AT GIVEN TEMPERATURE, PRESSURE AND CHEMICAL POTENTIAL

To conclude we choose as independent variables the temperature T, pressure P and chemical potential μ. An illustrative example is a gas in contact with a crystal of the same substance; the crystal is not considered as part of the system. Such a system is called *open*.

We now construct the triple sum

$$W\,(T,\,P,\,\mu,\,\xi) = \Sigma_r\,\Sigma_s\,\Sigma_t\,\Omega_{rst}\,(\xi)\;e^{-U_r/kT}\;e^{-PV_s/kT}\;e^{\mu N_t/kT} \qquad 2.\,07.\,1$$

where $\Omega_{rst}\,(\xi)$ denotes the number of states of energy U_r, volume V_s and content N_t corresponding to the given value of ξ and the triple summation extends over all sets of values of U_r, V_s, N_t corresponding to the given value of ξ. It can then be shown without any new assumptions that all the average properties of the system for the prescribed values of T, P, μ are correctly obtained by averaging over all values of ξ attaching to each a weight $W\,(T,\,P,\,\mu,\,\xi)$, this expression being the *partition function* or *thermodynamic probability of ξ for the given T, P, μ.*

For a macroscopic system W can in the usual way be replaced by its maximum term say

$$\Omega_m\left(\xi\right) e^{-U_m/kT} e^{-PV_m/kT}\, e^{\mu N_m/kT} \qquad \text{2.07.2}$$

If we now define a quantity $O\left(T, P, \mu, \xi\right)$ by

$$O\left(T, P, \mu, \xi\right) = k \ln W\left(T, P, \mu, \xi\right) \qquad \text{2.07.3}$$

we may for a macroscopic system replace (3) by

$$O\left(T, P, \mu, \xi\right) = k \ln \Omega_m\left(\xi\right) \quad \frac{U_m}{T} - \frac{PV_m}{T} + \frac{\mu N_n}{T} \qquad \text{2.07.4}$$

Moreover for a macroscopic system we have as usual

$$S = k \ln \Omega_m\left(\xi\right) \qquad \text{2.07.5}$$

$$U_{Av} = U_m \qquad \text{2.07.6}$$

$$V_{Av} = V_m \qquad \text{2.07.7}$$

$$N_{Av} = N_m \qquad \text{2.07.8}$$

Comparing (5) to (8) with (4) we find dropping subscripts that

$$O\left(T, P, \mu, \xi\right) = \frac{TS - U - PV + \mu N}{T} = 0 \qquad \text{2.07.9}$$

according to (1.35.4).

From the analogy between (3), (2.02.2), (2.04.13) and (2.06.2) we expect $O\left(T, P, \mu, \xi\right)$ to be a *characteristic function* for the variables T, P, and μ. According to (9) this characteristic function is identically zero. We now recall the Gibbs-Duhem relation (1.38.2)

$$S\mathrm{d}T - V\mathrm{d}P + \Sigma_i\, n_i\, \mathrm{d}\mu_i = 0 \qquad \text{2.07.10}$$

In a system of one component the sum $\Sigma_i\, n_i\, \mathrm{d}\mu_i$ reduces to $n\mathrm{d}\mu$ and if we denote by μ the chemical potential per molecule, instead of per mole as in chapter 1, (10) becomes

$$0 = S\mathrm{d}T - V\mathrm{d}P + N\mathrm{d}\mu \qquad \text{2.07.11}$$

showing that the characteristic function for the independent variables T, P, μ is indeed zero.

§ 2. 08 RECAPITULATION

We can now summarize the content of the several preceding sections*. For each selected set of three independent variables, other than ξ, a different kind of weighting factor w has to be attached to the microstates. The sum $\Sigma\, w$ for all microstates consistent with the prescribed values of the three chosen independent variables other than ξ and corresponding to a definite value of ξ is called the *partition function* or the *thermodynamic probability* for the prescribed values of ξ and the other three independent variables. Furthermore in each case $k \ln \Sigma w$ is a *characteristic function* for the chosen set of three independent variables other than ξ. These relationships are shown in table 2. 1.

TABLE 2 1

Independent variables	Weighting factor for each independent microstate	*Characteristic function* equal to $k \ln \Sigma\, w$
$U,\ V,\ N,\ \xi$	1	S
$T,\ V,\ N,\ \xi$	$e^{-U/kT}$	$J = -\,F/T$
$T,\ P,\ N,\ \xi$	$e^{-U/kT}\,e^{-PV/kT}$	$Y = -\,G/T$
$T,\ P,\ \mu,\ \xi$	$e^{-U/kT}\,e^{-PV/kT}\,e^{\mu N/kT}$	0

We emphasize again that each of the listed *characteristic functions* S, J, Y and zero is related to the corresponding *thermodynamic probability* according to

$$\text{characteristic function} = k \ln (\text{thermodynamic probability}).$$

The earliest and best known example of this form is Boltzmann's relation for $S\,(U, V, N, \xi)$, but the others and particularly that for $J\,(T, V, N, \xi)$ are in fact more useful.

Once again we mention that we have introduced J and Y largely because of their close analogy to S; for the benefit of the reader more familiar with F and G we again recall that

$$J = -\,F/T \qquad\qquad 2.\ 08.\ 1$$

$$Y = -\,G/T \qquad\qquad 2.\ 08.\ 2$$

It is a fundamental characteristic of a macroscopic system that any partition function may with trivial inaccuracy be replaced by its

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* Compare Guggenheim, *J. Chem. Phys.* 1939 **7** 103; *Forh. 5te Nordiske Kemikermode Köbenhavn* 1939 p. 205.

maximum term. It follows that the equilibrium value of ξ is that value which maximizes the characteristic function belonging to the chosen set of independent variables. The alternative equilibrium conditions

$$\text{for given } U \text{ and } V \text{ that } S \text{ is a } maximum \qquad 2.\,08.\,3$$

$$\text{for given } T \text{ and } V \text{ that } J \text{ is a } maximum \qquad 2.\,08.\,4$$

$$\text{for given } T \text{ and } P \text{ that } Y \text{ is a } maximum \qquad 2.\,08.\,5$$

thus obtained are precisely equivalent to (1. 43. 1), (1. 43. 3) and (1. 43. 4) respectively.

§ 2. 09. EXTENSION TO SEVERAL COMPONENTS. ABSOLUTE ACTIVITIES

We have hitherto restricted our exposition to systems of a single component purely for the sake of brevity. The extension to systems of several components is straightforward.

In particular for a system at given values of the independent variables T, P and the μ_i's, the weighting factor for each independent microstate will be

$$e^{-U/kT}\, e^{-PV/kT}\, \prod \lambda_i{}^{N_i} \qquad 2.\,09.\,1$$

where for brevity we have introduced quantities λ_i defined by

$$\lambda_i = e^{\mu_i/kT}$$

or

$$\mu_i = kT \ln \lambda_i \qquad 2.\,09.\,2$$

These quantities λ_i may be used instead of the μ_i's and are often more convenient. λ_i is called the *absolute activity* of the species i.

In later chapters we shall meet these formulae with a slightly different appearance in that Boltzmann's constant k will be replaced by another constant denoted by R. The explanation is simply that in this chapter μ denotes the chemical potential *per molecule*, whereas in all other chapters it denotes the chemical potential *per mole*. The ratio R/k is equal to the number L, called *Avogadro's number*, equal to the number of molecules in one mole.

§ 2. 10 ANTISYMMETRIC AND SYMMETRIC EIGENFUNCTIONS

In § 2. 01 we mentioned that it is often, though not always, possible to regard the units (molecules, atoms, ions, electrons) composing the system as almost independent. In this case each eigenfunction of the system can be expressed as a linear combination of products of the

eigenfunctions of all the units. We begin by considering the case that all the units are of the same kind. We denote the eigenfunctions of the units by φ and the eigenfunctions of the whole system by ψ. We have now to distinguish two cases.

If each unit is a fundamental particle (proton, neutron or electron) or is composed of an odd number of fundamental particles, then each eigenfunction ψ of the system is constructed by forming a determinant of the eigenfunctions of the individual units. For the sake of simplicity and brevity we consider a system consisting of only three units, numbered 1, 2, 3. The symbol φ_a (1) then denotes the eigenfunction of the unit 1 when in the state a. The eigenfunction $\psi_{a\beta\gamma}$ is then constructed as follows

$$\psi_{a\beta\gamma} \quad \begin{vmatrix} \varphi_a(1), & \varphi_\beta(1), & \varphi_\gamma(1) \\ \varphi_a(2), & \varphi_\beta(2), & \varphi_\gamma(2) \\ \varphi_a(3), & \varphi_\beta(3), & \varphi_\gamma(3) \end{vmatrix} \qquad \text{2. 10. 1}$$

We notice that if we interchange the states of any two units, ψ changes sign. We accordingly describe the eigenfunctions ψ as *antisymmetric* with respect to every pair of units. It follows at once that if any two of the states, a, β, γ are identical then $\psi_{a\beta\gamma}$ vanishes. Thus there is one independent ψ for each combination of three φ_a, φ_β, φ_γ provided a, β, γ are all different but none if any two of a, β, γ are the same.

If on the other hand each unit is a photon or is composed of an even number of fundamental particles (protons, neutrons, electrons), then each eigenfunction of the system is constructed from the eigenfunctions of the units by forming linear combinations similar to determinants, but in which all the terms are added. Thus in the case of only three units 1, 2, 3 the eigenfunction $\psi_{a\beta\gamma}$ is defined by

$$\psi_{a\beta\gamma} : \quad \begin{matrix} \varphi_a(1), & \varphi_\beta(1), & \varphi_\gamma(1) \\ \varphi_a(2), & \varphi_\beta(2), & \varphi_\gamma(2) \\ \varphi_a(3), & \varphi_\beta(3), & \varphi_\gamma(3) \end{matrix} \qquad \text{2. 10. 2}$$

which differs from (1) in that all the six terms are added. We notice that if we interchange the states of any two units, ψ remains unchanged. We accordingly describe the eigenfunction ψ as *symmetric* in all the units. It is clear that there is one independent ψ for every combination of three eigenfunctions φ_a, φ_β, φ_γ whether or not any two or more of a, β, γ are the same.

§ 2. 11 FERMI–DIRAC AND BOSE–EINSTEIN STATISTICS

Let us now consider a system containing N indistinguishable units and enquire how many eigenfunctions ψ of the system can be constructed out of g eigenfunctions φ of the units. There are two distinct problems with different answers according as ψ is to be antisymmetric or symmetric in the units.

In the case where ψ is to be antisymmetric, to obtain any such ψ at all g must be at least as great as N and the number of such eigenfunctions ψ is then

$$\frac{g!}{N!\,(g-N)!} \qquad \text{(antisymmetric, } g \geqslant N) \qquad 2.\,11.\,1$$

In the other case where ψ is to be symmetric, the number of such eigenfunctions ψ is

$$\frac{(g+N-1)!}{(g-1)!\,N!} \qquad \text{(symmetric)} \qquad 2.\,11.\,2$$

which, when $g \gg 1$, is not significantly different from the simpler expression

$$\frac{(g+N)!}{g!\,N!} \qquad \text{(symmetric, } g \gg 1) \qquad 2.\,11.\,3$$

It is of interest to note that when $g \gg N$, both (1) and (3) are nearly the same as

$$\frac{g^N}{N!} \qquad \text{(antisymmetric or symmetric, } g \gg N) \qquad 2.\,11.\,4$$

If now we translate the laws governing the average properties of the whole system outlined in §§ 2. 01—2. 09 into forms relating to the average distributions of the component units, we shall as a consequence of the difference between (1) and (2) find different results according as the eigenfunctions ψ are to be antisymmetric or symmetric in the units. These distribution laws take the simplest form if we choose as independent variables the temperature T, the volume V and the absolute activity λ. We shall now state these laws without any derivation.

Let ε_a denote the energy of a unit in the non-degenerate state a having the eigenfunction φ_a. Then if the unit is a fundamental particle (proton, neutron or electron) or is composed of an odd number of fundamental particles, the eigenfunction ψ must be antisymmetric

in the units and the average number N_a of units in the state a is found to be given by

$$\frac{N_a}{1 - N_a} = \lambda \, e^{-\epsilon_a / kT} \qquad\qquad 2.\,11.\,5$$

where λ denotes the *absolute activity* of the unit, T the absolute temperature and k Boltzmann's constant. This distribution law is called that of *Fermi–Dirac statistics*.

If on the other hand the unit is a photon or is composed of an even number of fundamental particles, the eigenfunction ψ must be symmetric in the units and the average number N_a of units in the state a is found to be given by

$$\frac{N_a}{1 + N_t} = \lambda \, e^{-\epsilon_a / kT} \qquad\qquad 2.\,11.\,6$$

This distribution law is called that of *Bose–Einstein statistics*.

It is to be noted that in both the cases of *Fermi–Dirac statistics* and *Bose–Einstein statistics* the average number N_a of units in each state is related simply and explicitly to the temperature T and the absolute activity λ, which we recall is related to the chemical potential μ by (2. 09. 2).

§ 2. 12 BOLTZMANN STATISTICS

Let the subscript $_0$ denote the state of lowest energy ϵ_0 and let us consider the case that

$$\lambda \, e^{-\epsilon_o / kT} \ll 1 \qquad\qquad 2.\,12.\,1$$

so that a fortiori

$$\lambda \, e^{-\epsilon_a / kT} \ll 1 \qquad \text{(all } a) \qquad 2.\,12.\,2$$

It then follows from either (2. 11. 5) or (2. 11. 6) that

$$N_a \ll 1 \qquad\qquad 2.\,12.\,3$$

We may then without loss of accuracy replace either (2. 11. 5) or (2. 11. 6) by

$$N_a = \lambda \, e^{-\epsilon_a / kT} \qquad\qquad 2.\,12.\,4$$

This distribution law is called that of *Boltzmann statistics*.

We now state without proof that in almost all the systems met in practice the condition (1) is satisfied. There are only two important exceptions. The first is the system of conducting electrons in a metal; these obey the Fermi–Dirac distribution law and will not be discussed

in this book. The other is the system of photons forming radiation; these obey the Bose–Einstein distribution law and will be discussed in chapter 13. Boltzmann statistics are sufficient for all the other systems to be met in this book and from here onwards we shall confine our attention to these.

§ 2. 13 PARTITION FUNCTIONS OF UNITS AND THERMODYNAMIC FUNCTIONS

For any system obeying Boltzmann statistics, we have according to (2. 12. 4)

$$N_a = \lambda \, e^{-\varepsilon_a/kT} \qquad\qquad 2. \ 13. \ 1$$

If we apply (1) to every state a and add, we obtain

$$N = \lambda \, \Sigma_a \, e^{-\varepsilon_a/kT} \qquad\qquad 2. \ 13. \ 2$$

so that

$$\mu = kT \ln \lambda = kT \ln \frac{N}{\Sigma_a \, e^{-\varepsilon_a/kT}} \qquad\qquad 2. \ 13. \ 3$$

The sum $\Sigma_a \, e^{-\varepsilon_a/kT}$ is called the *partition function of the units*. Its structure is similar to that of the *partition function of the whole system* for the independent variables T, V, N. Formula (3) is the basis for the evaluation of the thermodynamic functions in terms of the energies of all the states of the component units.

Formula (3) is equivalent to the formula for the *Massieu function J* and the *free energy F*

$$J = -\frac{F}{T} = k \ln \frac{(\Sigma_a \, e^{-\varepsilon_a/kT})^N}{N!} \qquad\qquad 2. \ 13. \ 4$$

If we compare (4) with (2. 04. 13) we see that the two are equivalent when we bear in mind that the factor $N!$ in the denominator in (4) is required to avoid counting as distinct states those obtainable from one another by a mere permutation of indistinguishable units.

The more general formula for a system containing more than one kind of units (molecules) is

$$J = -\frac{F}{T} = k \, \Sigma_i \ln \frac{(\Sigma_a \, e^{-\varepsilon_a/kT})^{N_i}}{N_i!} \qquad\qquad 2. \ 13. \ 5$$

§ 2. 14 SEPARABLE DEGREES OF FREEDOM

It is often the case that there is no appreciable interaction between two or more degrees of freedom of a unit. Such degrees of freedom are

said to be *separable*. Each eigenfunction φ may then be expressed as a product of the eigenfunctions for the several separable degrees of freedom, and the energy ε_a as the sum of the energies of the several separable degrees of freedom. It then follows immediately that the partition function of the unit can be expressed as the product of partition functions for its several separable degrees of freedom.

In particular the translational degrees of freedom of molecules are usually separable from the internal degrees of freedom. Among the internal degrees of freedom we here include rotational degrees of freedom as well as atomic vibrations, electronic and nuclear degrees of freedom. We may accordingly write for the partition function of a molecule

$$e^{-\varepsilon_a/kT} = e^{-\varepsilon_{tr}/kT} \, e^{-\varepsilon_{int}/kT} \qquad \qquad 2.\,14.\,1$$

where ε_{tr} denotes the energy of the translational degrees of freedom and ε_{int} the energy of the internal degrees of freedom. Substituting (1) into (2. 13. 5) we obtain for the Massieu function J and the free energy F

$$J = -\frac{F}{T} = k \, \Sigma_i \ln \frac{(\Sigma e^{-\varepsilon_{tr}/kT} \Sigma e^{-\varepsilon_{int}/kT})^{N_i}}{N_i!} \qquad \qquad 2.\,14.\,2$$

Alternatively we may write

$$J = J_{tr} + J_{int} \qquad \qquad 2.\,14.\,3$$

$$F = F_{tr} + F_{int} \qquad \qquad 2.\,14.\,4$$

$$J_{tr} = -\frac{F_{tr}}{T} = k \, \Sigma_i \ln \frac{(\Sigma e^{-\varepsilon_{tr}/kT})^{N_i}}{N_i!} \qquad \qquad 2.\,14.\,5$$

$$J_{int} = -\frac{F_{int}}{T} = k \, \Sigma_i N_i \ln \Sigma e^{-\varepsilon_{int}/kT} \qquad \qquad 2.\,14.\,6$$

where the subscript $_{tr}$ refers throughout to contributions from the translational degrees of freedom and the subscript $_{int}$ to contributions from the internal degrees of freedom.

§ 2. 15 CLASSICAL AND UNEXCITED DEGREES OF FREEDOM

It may happen that there are many energy levels less than kT. When this is the case, the sum which defines the partition function may without loss of accuracy be replaced by an integral, whose evaluation is often elementary. Such a degree of freedom is called a *classical degree of freedom*. Whether a particular degree of freedom

is classical depends on the temperature. Under ordinary conditions the translational and rotational degrees of freedom of the molecules in a gas are classical.

In the opposite case it may happen that the separation between the states of lowest energy level and those of the next energy level is several times greater than kT. The partition function then reduces effectively to the terms corresponding to the lowest energy level, that is to

$$g_0 \, e^{-\varepsilon_0/kT} \qquad\qquad 2.\,15.\,1$$

where ε_0 denotes the lowest energy level and g_0 denotes the number of states having this energy. Such degrees of freedom are called *unexcited degrees of freedom*. The contribution of each such unexcited degree of freedom to the free energy F is clearly

$$\varepsilon_0 - kT \ln g_0 \qquad\qquad 2.\,15.\,2$$

and the corresponding contribution to the entropy

$$k \ln g_0 \qquad\qquad 2.\,15.\,3$$

which we notice is independent of the temperature. Whether a particular degree of freedom is unexcited depends by definition on the temperature. At all the temperatures with which we are concerned all degrees of freedom internal to the atomic nucleus are unexcited. The electronic degrees of freedom of most molecules may also be regarded as unexcited at most of the temperatures which concern us; there are however a few exceptions, notably the molecule NO.

§ 2. 16 TRANSLATIONAL DEGREES OF FREEDOM

The translational degrees of freedom of a dilute gas may be regarded as classical. When the partition function for the translational degrees of freedom of a molecule is replaced by an integral and the integration is performed, one obtains

$$\left(\frac{2\pi mkT}{h^2} \right)^{\!\frac{3}{2}} V \qquad\qquad 2.\,16.\,1$$

where m denotes the mass of a molecule and V the volume in which it is enclosed; h denotes Planck's constant and k as usual Boltzmann's constant. Thus for a dilute gaseous mixture according to (2. 14. 5) we have

$$J_{\text{tr}} = -\frac{F_{\text{tr}}}{T} = k \, \Sigma_i \ln \frac{(2\pi m_i kT)^{\frac{3}{2}N_i} \, V^{N_i}}{h^{3N_i} \, N_i!} \qquad\qquad 2.\,16.\,2$$

Let us now consider the translational degrees of freedom in a crystal. We may regard each molecule as vibrating about an equilibrium position in the crystal lattice. Let us denote by q the partition function for a molecule attached to a given lattice position and for the moment let us imagine all the N molecules to be individually distinguishable but sufficiently alike so that any one can be interchanged with any other without destroying the crystal structure. Then the molecules can be permuted over the lattice positions in $N!$ ways, so that the partition function for the translational motion of the molecules of the whole crystal would be $N! \, q^N$. Actually the molecules are of course not individually distinguishable and we must consider only states whose eigenfunction is symmetric in molecules containing an even number of fundamental particles and antisymmetric in molecules containing an odd number of fundamental particles. In the simplest case when all the molecules in the crystal are of the same kind the number of states is thus reduced by a factor $N!$, which cancels the other $N!$, so that the partition function for the whole crystal becomes q^N. We thus have for a crystal of a pure substance

$$J_{tr} = -\frac{F_{tr}}{T} = k \ln q^N \qquad\qquad 2.\,16.\,3$$

Each molecule has at a given lattice position only one state of lowest translational energy and so at low temperatures q tends to unity. We therefore have for a crystal of a pure substance

$$J_{tr} = -\frac{F_{tr}}{T} \to 0 \qquad (T \to 0) \qquad\qquad 2.\,16.\,4$$

For a mixed crystal containing several distinguishable kinds of molecules, e.g. isotopes, the eigenfunctions have to be symmetric, or antisymmetric, only with respect to identical molecules. Hence we have to divide only by the product of all the $N_i!$ instead of by $N!$. We therefore have instead of (3)

$$J_{tr} = -\frac{F_{tr}}{T} = k \ln N! + k \, \Sigma_i \ln \frac{q_i^{N_i}}{N_i!} \qquad\qquad 2.\,16.\,5$$

where $N = \Sigma_i \, N_i$. It has been implicitly assumed that interchanging two molecules of different kinds in the crystal does not affect the partition function q_i of either of them. This assumption is justified

provided the molecules are sufficiently similar, e.g. isotopic. Since at low temperatures each q_i tends to unity it follows that

$$J_{tr} = -\frac{F_{tr}}{T} \rightarrow k \ln N! - k \Sigma_i \ln N_i! \quad (T \rightarrow 0) \qquad 2.\,16.\,6$$

§ 2. 17 THIRD PRINCIPLE OF THERMODYNAMICS

After this brief and admittedly incomplete sketch of statistical thermodynamics we recall the formulation of the *third principle of thermodynamics* which we adopted in § 1. 63.

By the standard methods of statistical thermodynamics it is possible to derive for certain entropy changes general formulae which cannot be derived from the zeroth, first or second principles of thermodynamics. In particular we can obtain formulae for entropy changes in highly disperse systems (i.e. gases), those in very cold systems (i.e. when $T \rightarrow 0$) and those associated with the mixing of very similar substances (e.g. isotopes).

We shall now briefly state these deductions from statistical thermodynamics without giving detailed derivations.

In the first place we consider the translational term in the thermodynamic functions of a highly disperse system, i.e. a gas, containing N_i molecules of type i having a mass m_i. The contributions to the Massieu function J and to the free energy F are given by

$$J_{tr} = -\frac{F_{tr}}{T} = k \Sigma_i \ln \frac{(2\pi m_i kT)^{\frac{3}{2}N_i} V^{N_i}}{h^{3N_i} N_i!} \qquad 2.\,17.\,1$$

The corresponding contribution S_{tr} to the entropy S is

$$S_{tr} = k \Sigma_i \ln \frac{(2\pi m_i kT)^{\frac{3}{2}N_i} V^{N_i}}{h^{3N_i} N_i!} + k \Sigma_i \tfrac{3}{2} N_i \qquad 2.\,17.\,2$$

In particular in a gaseous single substance

$$S_{tr} = k \ln \frac{(2\pi mkT)^{\frac{3}{2}N} V^N}{h^{3N} N!} + \tfrac{3}{2} Nk \qquad 2.\,17.\,3$$

Using Stirling's formula for large N

$$\ln N! = N \ln N - N \qquad 2.\,17.\,4$$

we can rewrite (3) as

$$\frac{S_{tr}}{Nk} = \ln \frac{(2\pi mkT)^{\frac{3}{2}} V}{h^3 N} + \tfrac{5}{2} \qquad 2.\,17.\,5$$

Anticipating the formula for the pressure P of a perfect gas

$$P = \frac{N}{V} kT \qquad \qquad 2.\,17.\,6$$

we can replace (5) by

$$\frac{S_{\text{tr}}}{Nk} = \ln \frac{(2\pi m)^{\frac{3}{2}} (kT)^{\frac{5}{2}}}{h^3 P} + \tfrac{5}{2} \qquad \qquad 2.\,17.\,7$$

We shall use the equivalent of formula (2. 17. 7) in § 4. 56.

Our second example is the translational term in the entropy of a crystal of a pure substance. As the temperature tends towards zero, this contribution tends to zero. We shall return to this law in § 4. 60.

Finally we consider the entropy of mixtures of very similar substances such as isotopes. If several very similar substances, such as isotopes, all at the same temperature and same number of molecules per unit volume are mixed, the temperature and number of molecules per unit volume being kept unchanged, the entropy is increased by ΔS given by

$$\frac{\Delta S}{k} = \ln N! - \Sigma_i \ln N_i! \qquad \qquad 2.\,17.\,8$$

where N_i denotes the number of molecules of the species i and $N = \Sigma_i N_i$ denotes the total number of molecules of all species. Using Stirling's formula (4), we can rewrite (8) as

$$\frac{\Delta S}{k} = \Sigma_i N_i \ln \frac{N}{N_i} \qquad \qquad 2.\,17.\,9$$

This applies to solids, and incidentally to liquids, as well as to gases, provided the various species are sufficiently similar, e.g. isotopic. We shall make use of this in § 4. 57.

When we meet these formulae again in chapter 4, the number of molecules N_i will be replaced by the number of moles n_i and correspondingly Boltzmann's constant k will be replaced by the gas constant R. In particular $N_i k$ becomes $n_i R$.

SOME RELATIONS OF GENERAL VALIDITY

§ 3. 01 IDENTITIES BETWEEN PARTIAL DIFFERENTIAL COEFFICIENTS

We begin this chapter by summarizing certain important properties of partial differential coefficients, which will frequently be required.

Let x, y and z denote three quantities any one of which is completely determined by the other two, so that we may regard any one as a function of the other two. Symbolically

$$z = z\,(x, y) \qquad\qquad 3.\,01.\,1$$

$$x = x\,(y, z) \qquad\qquad 3.\,01.\,2$$

$$y = y\,(z, x) \qquad\qquad 3.\,01.\,3$$

The partial differential coefficients are defined by relations such as

$$\left(\frac{\partial z}{\partial x}\right)_y = \underset{\delta x \to 0}{\mathrm{Lt}}\,\frac{z\,(x + \delta x,\, y) - z\,(x, y)}{\delta x} \qquad\qquad 3.\,01.\,4$$

From this definition it follows immediately that

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial z}\right)_y = 1 \qquad\qquad 3.\,01.\,5$$

and there are of course two other similar relations obtained by permuting x, y, z.

Subject to certain conditions concerning the smoothness of the function $z\,(x, y)$ which will always be fulfilled in the physical applications, the order of successive differentiations of $z\,(x, y)$ is immaterial. In particular

$$\frac{\partial}{\partial x}\left\{\left(\frac{\partial z}{\partial y}\right)_x\right\}_y = \left\{\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)_y\right\}_x \qquad\qquad 3.\,01.\,6$$

or more briefly

$$\frac{\partial}{\partial x}\,\frac{\partial z}{\partial y} = \frac{\partial}{\partial y}\,\frac{\partial z}{\partial x} \qquad\qquad 3.\,01.\,7$$

We shall make much use of this relation and for the sake of brevity shall refer to it as the *cross-differentiation identity*.

When we differentiate (1), (2) and (3), using the definitions of partial differential coefficients, we obtain

$$\mathrm{d}z = \left(\frac{\partial z}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial z}{\partial y}\right)_x \mathrm{d}y \qquad\qquad 3.01.8$$

$$\mathrm{d}x = \left(\frac{\partial x}{\partial y}\right)_z \mathrm{d}y + \left(\frac{\partial x}{\partial z}\right)_y \mathrm{d}z \qquad\qquad 3.01.9$$

$$\mathrm{d}y = \left(\frac{\partial y}{\partial z}\right)_x \mathrm{d}z + \left(\frac{\partial y}{\partial x}\right)_z \mathrm{d}x \qquad\qquad 3.01.10$$

Substituting (9) into (8) we obtain

$$\mathrm{d}z = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial z}\right)_y \mathrm{d}z + \left\{ \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x \right\} \mathrm{d}y \qquad 3.01.11$$

and using (5)

$$\mathrm{d}z = \mathrm{d}z + \left\{ \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x \right\} \mathrm{d}y \qquad 3.01.12$$

or since $\mathrm{d}y$ is arbitrary

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x = 0 \qquad\qquad 3.01.13$$

We can rewrite (13) in the alternative form

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial z}{\partial y}\right)_x \bigg/ \left(\frac{\partial z}{\partial x}\right)_y \qquad\qquad 3.01.14$$

or, by using relations of the form (5), in the symmetrical form

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \qquad\qquad 3.01.15$$

All the above differential relations between x, y, z remain valid even when there are further variables provided all the remaining variables are held constant. For example an extension of (15) is

$$\left(\frac{\partial x}{\partial y}\right)_{z,u,v} \left(\frac{\partial y}{\partial z}\right)_{x,u,v} \left(\frac{\partial z}{\partial x}\right)_{y,u,v} = -1 \qquad\qquad 3.01.16$$

Among the useful applications of (7) there will be cases where one

of the independent variables is the extent of reaction defined in § 1. 50. Thus

$$\frac{\partial}{\partial x}\frac{\partial z}{\partial \xi} = \frac{\partial}{\partial \xi}\frac{\partial z}{\partial x} \qquad 3.\ 01.\ 17$$

The equivalent relation in alternative notation is

$$\frac{\partial}{\partial x}\Delta z = \Delta \frac{\partial z}{\partial x} \qquad 3.\ 01.\ 18$$

where the operator symbol Δ, as usual, denotes the increase of any quantity when the particular change being considered takes place. As just one of many concrete examples of (18) we may mention

$$\left(\frac{\partial \Delta H}{\partial P}\right)_T = \Delta \left(\frac{\partial H}{\partial P}\right)_1 \qquad 3.\ 01.\ 19$$

There is a further relation, which we shall require, between the four quantities w, x, y, z such that any two completely determine the other two. If we regard w firstly as a function of x, y and secondly as a function of x, z we have

$$dw = \left(\frac{\partial w}{\partial x}\right)_y dx + \left(\frac{\partial w}{\partial y}\right)_x dy \qquad 3.\ 01.\ 20$$

$$dw = \left(\frac{\partial w}{\partial x}\right)_z dx + \left(\frac{\partial w}{\partial z}\right)_x dz \qquad 3.\ 01.\ 21$$

Substituting from (8) into (21) we obtain

$$dw = \left\{ \left(\frac{\partial w}{\partial x}\right)_z + \left(\frac{\partial w}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y \right\} dx + \left(\frac{\partial w}{\partial z}\right)_x \left(\frac{\partial z}{\partial y}\right)_x dy \qquad 3.\ 01.\ 22$$

Comparing (22) with (20) and equating coefficients of the independent variations dx, dy we obtain

$$\left(\frac{\partial w}{\partial x}\right)_y = \left(\frac{\partial w}{\partial x}\right)_z + \left(\frac{\partial w}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y \qquad 3.\ 01.\ 23$$

$$\left(\frac{\partial w}{\partial y}\right)_x = \left(\frac{\partial w}{\partial z}\right)_x \left(\frac{\partial z}{\partial y}\right)_x \qquad 3.\ 01.\ 24$$

The relation (24) is rather obvious; for, since x is held constant

throughout, we may ignore x and think of w, y, z as three quantities any one of which determines the other two. Then evidently

$$\frac{\mathrm{d}w}{\mathrm{d}y} = \frac{\mathrm{d}w}{\mathrm{d}z}\frac{\mathrm{d}z}{\mathrm{d}y} \qquad \text{3. 01. 25}$$

and (24) merely states that this remains true when w, y, z also depend on x provided x is kept constant. The relation (23) is more important and will be required.

§ 3. 02 CHOICE OF INDEPENDENT VARIABLES

For practical purposes the most convenient independent variables, other than the composition, to describe any single phase are, usually, temperature and pressure. We shall therefore require to express most thermodynamic properties as functions of T, P and shall be interested in their partial derivatives with respect to T and P. In the case of gases, in contrast to liquids and solids, it is sometimes convenient to choose as independent variables T, V instead of T, P. We shall accordingly also require to express thermodynamic properties as functions of T, V and shall be interested in their partial derivatives with respect to T and V.

§ 3. 03 COEFFICIENT OF THERMAL EXPANSION AND ISOTHERMAL COMPRESSIBILITY

If we regard the volume of a phase of fixed composition as a function of temperature and pressure, we have

$$\mathrm{d}V = \left(\frac{\partial V}{\partial T}\right)_P \mathrm{d}T + \left(\frac{\partial V}{\partial P}\right)_T \mathrm{d}P \qquad \text{3. 03. 1}$$

We define a the *coefficient of (cubic) thermal expansion*, by

$$a = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \text{3. 03. 2}$$

and $\varkappa$ the (isothermal) *compressibility* by

$$\varkappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad \text{3. 03. 3}$$

Substituting (2) and (3) into (1) we obtain

$$dV = aVdT - \varkappa VdP \qquad 3.03.4$$

01

$$d \ln V = adT - \varkappa dP \qquad 3.03.5$$

Alternatively if we choose to regard P as a function of T, V, we have

$$dP = \frac{a}{\varkappa} dT - \frac{1}{\varkappa V} dV \qquad 3.03.6$$

By applying the cross-differentiation identity (3.01.7) to (5), we obtain

$$\frac{\partial a}{\partial P}\bigg)_T = -\left(\frac{\partial \varkappa}{\partial T}\right)_P \qquad 3.03.7$$

§ 3.04 MAXWELL'S RELATIONS

For a closed system in the absence of chemical reactions and in particular for a single phase of fixed content, formulae (1.31.4) and (1.31.6) reduce to

$$dF = -SdT - PdV \qquad 3.04.1$$

$$dG = -SdT + VdP \qquad 3.04.2$$

Making use of the cross differentiation identity (3.01.7), we have

$$\frac{\partial S}{\partial V}\bigg)_T = \left(\frac{\partial P}{\partial T}\right)_V = \frac{a}{\varkappa} \qquad 3.04.3$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -aV \qquad 3.04.4$$

These two relations, due to Maxwell [*], are important since they express the dependence of entropy on volume or pressure in terms of the more readily measurable quantities a and $\varkappa$.

§ 3.05 DEPENDENCE OF THERMODYNAMIC FUNCTIONS ON PRESSURE

If, as will usually be our choice, we take as independent variables, other than the composition of each phase, the temperature T and the pressure P the relevant characteristic function is the Gibbs function G and according to (1.33.8) we have

$$\left(\frac{\partial G}{\partial P}\right)_T = V \qquad 3.05.1$$

[*] Maxwell, *Theory of Heat* 1885 ed. p. 169.

We also have Maxwell's relation (3. 04. 4)

$$\left(\frac{\partial S}{\partial P}\right)_T = -aV \qquad 3.\ 05.\ 2$$

Since the heat function H is related to G and S by

$$H = G + TS \qquad 3.\ 05.\ 3$$

we have using (1) and (2)

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial G}{\partial P}\right)_T + T\left(\frac{\partial S}{\partial P}\right)_T = V\left(1 - aT\right) \qquad 3.\ 05.\ 4$$

When we use the independent variables T, P the functions F, U are much less important than G, H. If nevertheless we should require their dependence on the pressure, it is readily derived as follows. By definition

$$F = G - PV \qquad 3.\ 05.\ 5$$

and so by differentiation with respect to P at constant T we obtain

$$\left(\frac{\partial F}{\partial P}\right)_T = \left(\frac{\partial G}{\partial P}\right)_T - V - P\left(\frac{\partial V}{\partial P}\right)_T = -P\left(\frac{\partial V}{\partial P}\right)_T \qquad 3.\ 05.\ 6$$

using (1). Substituting (3. 03. 3) into (6) we obtain

$$\left(\frac{\partial F}{\partial P}\right)_T = \varkappa PV \qquad 3.\ 05.\ 7$$

Finally since by definition

$$H - U = G - F \qquad 3.\ 05.\ 8$$

we obtain from (1), (4) and (7)

$$\left(\frac{\partial U}{\partial P}\right)_T = V\left(\varkappa P - aT\right) \qquad 3.\ 05.\ 9$$

§ 3. 06 GIBBS–HELMHOLTZ RELATION

If, as will usually be our choice, we take as independent variables, other than the composition of each phase, the temperature and the pressure we have for the temperature dependence of the relevant characteristic function G according to (1. 33. 6)

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad 3.\ 06.\ 1$$

If we compare this with the definition of G, namely

$$G = H - TS \qquad 3.06.2$$

and eliminate S, we obtain

$$H = G - T \left(\frac{\partial G}{\partial T}\right)_P \qquad 3.06.3$$

If we apply this relation to the final state II and to the initial state I in any isothermal process and take the difference, we obtain

$$\Delta H = \Delta G - T \left(\frac{\partial \Delta G}{\partial T}\right)_{P^I, P^{II}} \qquad 3.06.4$$

where P^I, P^{II} denote the initial and final pressures respectively. Formula (4) is known as the *Gibbs–Helmholtz relation*. This name is also sometimes given to formula (3)

By simple transformation we can rewrite these formulae as

$$\left\{\frac{\partial (G/T)}{\partial T}\right\}_P = -\frac{H}{T^2} \qquad 3.06.5$$

$$\frac{\partial (\Delta G/T)}{\partial T}\bigg|_{P^I, P^{II}} = -\frac{\Delta H}{T^2} \qquad 3.06.6$$

or alternatively as

$$\left\{\frac{\partial (G/T)}{\partial (1/T)}\right\}_P = H \qquad 3.06.7$$

$$\frac{\partial (\Delta G/T)}{\partial (1/T)}\bigg|_{P^I, P^{II}} = \Delta H \qquad 3.06.8$$

If instead of the Gibbs function G, we use the Planck function Y defined by

$$Y = -G/T \qquad 3.06.9$$

we have

$$\left\{\frac{\partial Y}{\partial (1/T)}\right\}_P = -H \qquad 3.06.10$$

$$\frac{\partial \Delta Y}{\partial (1/T)}\bigg|_{P^I, P^{II}} = -\Delta H \qquad 3.06.11$$

§ 3.07 DEPENDENCE OF THERMODYNAMIC FUNCTIONS ON T, V

As already stated, it is usually convenient to take T, P as independent variables. Only in the case of gases is it sometimes convenient

to use instead the independent variables T, V. The dependence of the various thermodynamic functions on these variables is readily obtained and we give the chief results for a phase of fixed composition in the order in which they are conveniently derived without however giving details of the derivations.

$$dF = -SdT - PdV \qquad\qquad 3.07.1$$

$$dP = \frac{a}{\varkappa}dT - \frac{1}{\varkappa V}dV \qquad\qquad 3.07.2$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \frac{a}{\varkappa}dV \qquad\qquad 3.07.3$$

$$dU = T\left(\frac{\partial S}{\partial T}\right) dT + \left(\frac{aT}{\cdots} - P\right)dV \qquad\qquad 3.07.4$$

$$d\left(\frac{F}{T}\right) = -\frac{U}{T^2}dT - \frac{P}{T}dV \qquad\qquad 3.07.5$$

$$dJ = \frac{U}{T^2}dT + \frac{P}{T}dV \qquad\qquad 3.07.6$$

By applying (5) or (6) to the final state II and the initial state I of an isothermal process and taking the difference we obtain the analogues of the Gibbs–Helmholtz relation

$$\frac{\partial\,(\Delta F/T)}{\partial T}\Big|_{V^I,V^{II}} = \frac{\Delta U}{T^2} \qquad\qquad 3.07.7$$

$$\frac{\partial\Delta J}{\partial T}\Big|_{V^I,V^{II}} = \frac{\Delta U}{T^2} \qquad\qquad 3.07.8$$

These may also be written in the forms

$$\left\{\frac{\partial\,(\Delta F/T)}{\partial\,(1/T)}\right\}_{V^I,V^{II}} = \Delta U \qquad\qquad 3.03.9$$

$$\left\{\frac{\partial\Delta J}{\partial\,(1/T)}\right\}_{V^I,V^{II}} = -\Delta U \qquad\qquad 3.07.10$$

§ 3.08 USE OF JACOBIANS

Many thermodynamic identities, including those obtained in the preceding sections, can be obtained rapidly and elegantly by the use of

Jacobians. The procedures are due to Shaw [*], who has shown how to apply them to obtain a tremendous number of identities, some important, others merely amusing. We shall here give a brief sketch of the method, which we shall illustrate by a few simple examples. We would however emphasize that all the simple and most important relations are deduced in this book without using Jacobians, so that the reader not interested in their use may omit this section which does not affect the rest of the book.

We recall that Jacobians are defined by

$$\frac{\partial (x, y)}{\partial (\alpha, \beta)} = \frac{\partial (y, x)}{\partial (\alpha, \beta)} = \left(\frac{\partial x}{\partial \alpha}\right)_\beta \left(\frac{\partial y}{\partial \beta}\right)_\alpha - \left(\frac{\partial x}{\partial \beta}\right)_\alpha \left(\frac{\partial y}{\partial \alpha}\right)_\beta \qquad 3.\ 08.\ 1$$

and that they obey the multiplicative law

$$\frac{\partial (x, y)}{\partial (u, v)} \frac{\partial (u, v)}{\partial (\alpha, \beta)} = \frac{\partial (x, y)}{\partial (\alpha, \beta)} \qquad 3.\ 08.\ 2$$

which can be derived by simple geometrical or algebraical considerations on transformation of coordinates.

As particular cases of (1) we have

$$\left(\frac{\partial x}{\partial \alpha}\right)_\beta = \frac{\partial (x, \beta)}{\partial (\alpha, \beta)} = -\frac{\partial (\beta, x)}{\partial (\alpha, \beta)} \qquad 3.\ 08.\ 3$$

$$\left(\frac{\partial y}{\partial \beta}\right)_\alpha = \frac{\partial (\alpha, y)}{\partial (\alpha, \beta)} = -\frac{\partial (y, \alpha)}{\partial (\alpha, \beta)} \qquad 3.\ 08.\ 4$$

Using (3) and (4) we derive from (2)

$$\left(\frac{\partial x}{\partial z}\right)_y = \frac{\partial (x, y)}{\partial (z, y)} = \frac{\partial (x, y)}{\partial (\alpha, \beta)} \bigg/ \frac{\partial (z, y)}{\partial (\alpha, \beta)} \qquad 3.\ 08.\ 5$$

We now replace α, β by the pair of quantities which we regard as the usually most convenient independent variables, namely the temperature T and the pressure P. We further introduce the following new notation

$$J (x, y) \equiv \frac{\partial (x, y)}{\partial (T, P)} \equiv \left(\frac{\partial x}{\partial T}\right)_P \left(\frac{\partial y}{\partial P}\right)_T - \left(\frac{\partial x}{\partial P}\right)_T \left(\frac{\partial y}{\partial T}\right)_P \qquad 3.\ 08.\ 6$$

In particular we have

[*] Shaw, *Phil. Trans. Roy. Soc.* A 1935 **234** 299.

$$\left(\frac{\partial x}{\partial T}\right)_P = J\,(x,\,P) = -\,J\,(P,\,x) \qquad\qquad 3.\,08.\,7$$

$$\left(\frac{\partial x}{\partial P}\right)_T = -\,J\,(x,\,T) = J\,(T,\,x) \qquad\qquad 3.\,08.\,8$$

Using our new notation we have instead of (5)

$$\left.\frac{\partial x}{\partial z}\right)_y = \frac{J\,(x,\,y)}{J\,(z,\,y)} \qquad\qquad 3.\,08.\,9$$

The relations (6) and (9) together enable us to express any quantity of the type $(\partial x/\partial z)_y$ in terms of the partial differential coefficients of $x,\,y,\,z$ with respect to $T,\,P$.

We shall illustrate by two examples, the first a useful one, the second far fetched. We have

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{J\,(T,\,H)}{J\,(P,\,H)} = -\left(\frac{\partial H}{\partial P}\right)_T \Big/ \left(\frac{\partial H}{\partial T}\right)_P \qquad\qquad 3.\,08.\,10$$

a relation which we shall meet again in § 4. 17, where it is derived more simply by using (3. 01. 14).

We now take a more complicated, and less useful, example

$$\left(\frac{\partial H}{\partial G}\right)_F = \frac{J\,(H,\,F)}{J\,(G,\,F)} = \frac{\left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial F}{\partial P}\right)_T - \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial F}{\partial T}\right)}{\left(\frac{\partial G}{\partial T}\right)_P \left(\frac{\partial F}{\partial P}\right)_T - \left(\frac{\partial G}{\partial P}\right)_T \left(\frac{\partial F}{\partial T}\right)_P} \qquad\qquad 3.\,08.\,11$$

in which all the derivatives on the right can be expressed in terms of readily measurable quantities. Thus the derivatives of G occurring on the right of (11) have the simple values

$$\left(\frac{\partial G}{\partial T}\right)_P = -\,S \qquad\qquad 3.\,08.\,12$$

$$\left.\frac{\partial G}{\partial P}\right)_T = V \qquad\qquad 3.\,08.\,13$$

The values of the derivatives of H are given by

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial\,[G + TS]}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P \qquad\qquad 3.\,08.\,14$$

$$\frac{\partial H}{\partial P}\bigg)_T = \left(\frac{\partial\,[G + TS]}{\partial P}\right)_T = \left(\frac{\partial G}{\partial P}\right)_T + T\left(\frac{\partial S}{\partial P}\right)_T = V\,(1 - aT) \quad 3.\,08.\,15$$

Similarly the values of the derivatives of F are given by

$$\left(\frac{\partial F}{\partial T}\right)_P = \left(\frac{\partial\,[G - PV]}{\partial T}\right)_P = \left(\frac{\partial G}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial T}\right)_P = -(S + aVP) \quad 3.\,08.\,16$$

$$\left(\frac{\partial F}{\partial P}\right)_T = \left(\frac{\partial\,[G - PV]}{\partial P}\right)_T = -P\left(\frac{\partial V}{\partial P}\right)_T = \varkappa PV \quad 3.\,08.\,17$$

Now substituting (12) to (17) into (11) we obtain

$$\left(\frac{\partial H}{\partial G}\right)_F = \frac{C\varkappa PV + V\,(1 - aT)\,(S + aVP)}{-S\varkappa PV + V\,(S + aVP)}$$

$$= \frac{C\varkappa P + (1 - aT)\,(S + aVP)}{-S\varkappa P + (S + aVP)} \qquad 3.\,08.\,18$$

where we have used C to denote $(\partial H/\partial T)_P$.

These illustrative examples by no means exhaust the uses to which Jacobians can be put. The reader who is interested is referred to the original papers by Shaw.

§ 3. 09 REVERSIBLE CYCLES

Suppose a system is taken through a complete cycle of states. Then as its final state is identical with its initial state, its entropy must obviously be the same at the end as at the beginning. Thus

$$\Delta S = 0 \qquad \text{(any cycle)} \qquad 3.\,09.\,1$$

If at all stages the system is in equilibrium, so that no irreversible (natural) change takes place, then

$$\Delta S = \Sigma_t \frac{q_t}{T_t} \qquad \text{(reversible changes)} \qquad 3\;09.\,2$$

where q_t denotes the heat absorbed at the temperature T_t and the summation extends over all the temperatures through which the system passes. Substituting (2) into (1) we obtain

$$\Sigma_t \frac{q_t}{T_t} = 0 \qquad \text{(reversible cycle)} \qquad 3.\,09.\,3$$

Evidently, since T_t is always positive, some of the q_t's must be positive

and some negative. It is convenient here to modify our notation so as to distinguish between the positive and negative q_i's. We accordingly replace (3) by

$$\Sigma_r \frac{q_r}{T_r} = \Sigma_s \frac{Q_s}{T_s} \qquad \text{(reversible cycle)} \qquad 3.\,09.\,4$$

where each q_r is a positive quantity of heat taken in at the temperature T_r and each Q_s is a positive quantity of heat given out at the temperature T_s.

According to the first principle of thermodynamics the work $-w$ done by the system during the cycle is given by

$$-w = \Sigma_i\, q_i = \Sigma_r\, q_r - \Sigma_s\, Q_s \qquad 3.\,09.\,5$$

The ratio η defined by

$$\eta = \frac{-w}{\Sigma_r\, q_r} = \frac{\Sigma_r\, q_r - \Sigma_s\, Q_s}{\Sigma_r\, q_r} = 1 - \frac{\Sigma_s\, Q_s}{\Sigma_r\, q_r} \qquad 3.\,09.\,6$$

is called by engineers the *thermodynamic efficiency* of the cycle.

Let us suppose that there is a maximum temperature T_{max} and a minimum temperature T_{min}, between which temperatures the cycle is confined. The following question arises. Subject to this restriction on the temperatures, what is the maximum possible value of η? The answer is obviously obtained by making

$$T_r = T_{max} \qquad \text{(all } r) \qquad 3.\,09.\,7$$

$$T_s = T_{min} \qquad \text{(all } s) \qquad 3.\,09.\,8$$

This means that positive absorption of heat occurs only at the highest emperature T_{max} and positive loss of heat occurs only at the lowest temperature T_{min}. No heat is exchanged with the surroundings at any temperature intermediate between T_{max} and T_{min}. In other words the passages from T_{max} to T_{min} and the reverse are adiabatic. Thus the cycle consists entirely of isothermal absorption of heat at T_{max}, isothermal emission of heat at T_{min}, and adiabatic changes from T_{max} to T_{min} and from T_{min} to T_{max}. Such a cycle was first considered by Carnot and is called *Carnot's cycle*.

For Carnot's cycle we have by substituting from (7) and (8) into (4)

$$\frac{\Sigma_r\, q_r}{T_{max}} = \frac{\Sigma_s\, Q_s}{T_{min}} \qquad \text{(Carnot's cycle)} \qquad 3.\,09.\,9$$

Now substituting from (9) into (6) we obtain

$$\eta = 1 - \frac{T_{\min}}{T_{\max}} \quad \text{(Carnot's cycle)} \qquad 3.\,09.\,10$$

There is sometimes confusion between Carnot's cycle and reversible cycles. It will be observed that Carnot's cycle is a very special case of a reversible cycle.

A completely isothermal cycle is a special case of Carnot's cycle. For such a cycle

$$T_{\max} = T_{\min} = T \qquad \text{(isothermal cycle)} \qquad 3.\,09.\,11$$

$$\Sigma_r\, q_r = \Sigma_s\, Q_s \qquad \text{(isothermal cycle)} \qquad 3.\,09.\,12$$

$$w = 0 \qquad \text{(isothermal cycle)} \qquad 3.\,09.\,13$$

$$\eta = 0 \qquad \text{(isothermal cycle)} \qquad 3.\,09.\,14$$

Formula (13) is known as *Moutier's theorem.*

We shall have no occasion to make any further reference to cycles. They are important in engineering thermodynamics for the treatment of engines and refrigerators, but these fall outside the subject-matter of this book.

SYSTEMS OF A SINGLE COMPONENT

§ 4. 01 THERMAL CONDITION OF INTERNAL STABILITY

Consider a homogeneous pure single substance, that is to say a single phase of one component. Let its entropy be S, its volume V and its energy U. Imagine one half of the mass of this phase to change so as have an entropy $\frac{1}{2}(S + \delta S)$ and volume $\frac{1}{2}V$ while the other half changes so as to have an entropy $\frac{1}{2}(S - \delta S)$ and volume $\frac{1}{2}V$. According to Taylor's expansion the energy of the first half becomes

$$\frac{1}{2}\left\{ U + \frac{\partial U}{\partial S} \delta S + \frac{1}{2}\frac{\partial^2 U}{\partial S^2}(\delta S)^2 \right\} \qquad 4.\,01.\,1$$

when we neglect small quantities of third and higher orders; all partial differentiations in (1) are at constant V. The energy of the second half becomes similarly

$$\frac{1}{2}\left\{ U - \frac{\partial U}{\partial S} \delta S + \frac{1}{2}\frac{\partial^2 U}{\partial S^2}(\delta S)^2 \right\} \qquad 4.\,01.\,2$$

Hence by addition the energy of the whole system has increased by the second order small quantity

$$\Bigg)_V (\delta S)^2 \qquad 4.\,01.\,3$$

while the total entropy and volume remain unchanged. Now a condition for a system to be in *stable* equilibrium is that, for given values of the entropy and the volume, the energy should be a *minimum*. If then the original state of the system was *stable*, the change considered must lead to an *increase* of energy and the expression (3) must be positive. Hence we obtain as a necessary condition for stable equilibrium

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_V > 0 \qquad 4.\,01.\,4$$

Since according to (1. 29. 4) or (1. 30. 1)

$$\left(\frac{\partial U}{\partial S}\right)_V = T \qquad\qquad 4.\,01.\,5$$

we can replace (4) by

$$\left(\frac{\partial S}{\partial T}\right)_V > 0 \qquad\qquad 4.\,01.\,6$$

The physical meaning of (6) is that when at constant volume heat is supplied to a stable phase its temperature is raised.

§ 4. 02 HYDROSTATIC CONDITION OF INTERNAL STABILITY

Consider again a single phase of one component. Let its temperature be T, its volume V and its free energy F. Imagine half of the mass to change so as to have a volume $\frac{1}{2}(V + \delta V)$, and the other half to change so as to have a volume $\frac{1}{2}(V - \delta V)$, the temperature remaining uniform and unchanged. Then by an argument precisely analogous to that of the previous section we find that the free energy of the whole system has increased by the second order small quantity

$$\frac{1}{2}\left(\frac{\partial^2 F}{\partial V^2}\right)_T (\delta V)^2 \qquad\qquad 4.\,02.\,1$$

while the temperature and total volume are unchanged. Now a condition for a system to be in *stable* equilibrium is that for given values of temperature and volume, the free energy should be a *minimum*. If then the original state of the system was *stable*, the change considered must lead to an *increase* of free energy and the expression (1) must be positive. Hence we obtain as a necessary condition for stable equilibrium

$$\left(\frac{\partial^2 F}{\partial V^2}\right)_T > 0 \qquad\qquad 4.\,02.\,2$$

Since according to (1. 31. 4)

$$\left(\frac{\partial F}{\partial V}\right)_T = -P \qquad\qquad 4.\,02.\,3$$

we can replace (2) by

$$\left(\frac{\partial V}{\partial P}\right)_T < 0 \qquad\qquad 4.\,02.\,4$$

or using (3. 03. 3), since V is always positive,

$$\varkappa > 0 \qquad\qquad 4.\,02.\,5$$

This means that when the pressure of a stable phase is increased, the volume must decrease. Whilst this condition is necessary we shall see in § 4. 49 that it is not sufficient for stability

§ 4. 03 OTHER CONDITIONS OF INTERNAL STABILITY

By reasoning similar to that of the two previous sections, we can obtain other conditions necessary for internal equilibrium of a single phase of one component. In particular we could obtain the conditions

$$\left(\frac{\partial S}{\partial T}\right)_P > 0 \qquad\qquad 4.\,03.\,1$$

and

$$\left(\frac{\partial V}{\partial P}\right)_S < 0 \qquad\qquad 4.\,03.\,2$$

Such other conditions are however not independent but can be derived from the previous ones. In fact we shall in § 4. 09 find that

$$\left.\frac{\partial S}{\partial T}\right)_P \geqslant \left(\frac{\partial S}{\partial T}\right)_V \qquad\qquad 4.\,03.\,3$$

so that (1) follows from (4. 01. 6). We shall also find in § 4. 26 that

$$\left.\frac{\partial V}{\partial P}\right)_S \Big/ \left(\frac{\partial V}{\partial P}\right)_T = \left(\frac{\partial S}{\partial T}\right)_V \Big/ \left(\frac{\partial S}{\partial T}\right)_P \qquad\qquad 4.\,03.\,4$$

so that (2) follows from (4. 02. 4) with (4. 01. 6) and (1).

§ 4. 04 DEPENDENCE OF ENTROPY ON TEMPERATURE

The experimental determination of entropy and absolute temperature are interlinked. We have not yet described how either can be directly or conveniently measured. In § 4. 13 we shall describe an especially convenient way of measuring absolute temperature. Anticipating this result, that is to say assuming we have a thermometer which measures absolute temperature, we shall now describe how we can determine the dependence of entropy on temperature at constant pressure.

For a single closed phase, we have according to (1. 31. 5)

$$dH = TdS + VdP \qquad\qquad 4.\,04.\,1$$

or if we keep the pressure constant

$$dH = TdS \qquad (P \text{ const.}) \qquad\qquad 4.\,04.\,2$$

If then we supply heat q to a single component system, since the change in the system must be reversible, quite regardless of whether the process of supplying the heat is reversible (see § 1. 15), we have

$$q = dH = TdS \qquad (P \text{ const.}) \qquad 4.\,04.\,3$$

Furthermore if we supply the heat by means of an electric element, the heat will be equal to the electrical work done on the element. To be precise, if the potential difference across the element is E and the current flowing is i, then in a time t the heat given up by the element to the system is Eit. Since E, i and t are all measurable we can calculate q. We see then that, apart from experimental difficulties, there is no difficulty in principle in measuring increases of H. As already mentioned we are postulating, in anticipation of § 4. 13, the availability of a thermometer which measures T. We thus obtain a direct experimental relationship between T and H, or rather changes in H which itself contains an arbitrary additive constant.

As an illustration we show in fig. 4. 1 the experimental data [*] for one mole of H_2O at a constant pressure of one atmosphere. The first curve on the left applies to ice from 0 °K to 273.15 °K, at which temperature the ice melts; the value of the heat function then rises at constant temperature by an amount equal to the molar heat of fusion. As this change would run off the paper the scale of the curve for the liquid has been shifted downwards by 6.4 kJ mole⁻¹. This curve on the right of the figure runs from 273.15 °K to 373.15 °K at which temperature the water boils; the value of the heat function again rises at constant temperature and runs off the diagram.

In fig. 4. 2 we show the data in a somewhat different form, $(\partial H/\partial T)_P$ being now plotted against $\ln T$. The three separate curves apply to ice, liquid water and steam respectively. From (2) we have

$$S = \int dS = \int \frac{dH}{T} = \int \left(\frac{\partial H}{\partial T}\right)_P \frac{dT}{T} = \int \left(\frac{\partial H}{\partial T}\right)_P d \ln T \qquad 4.\,04.\,4$$

We see then that apart from an arbitrary constant the entropy of ice at a temperature T is equal to the area under the part of the curve to the left of T. In particular the entropy of ice at the fusion point exceeds that at 0 °K by an amount corresponding to the whole area under the ice curve. This amounts to 38.09 J deg⁻¹ mole⁻¹.

When the ice changes to liquid water there is an increase of entropy

[*] Giauque and Stout, *J. Amer. Chem Soc.* 1936 **58** 1144.

called the *entropy of fusion* equal to the heat of fusion divided by the temperature. Thus

$$\Delta S = \frac{\Delta H}{T} = \frac{6007 \text{ J mole}^{-1}}{273.15 \text{ deg}} = 21.99 \text{ J deg}^{-1} \text{ mole}^{-1}$$
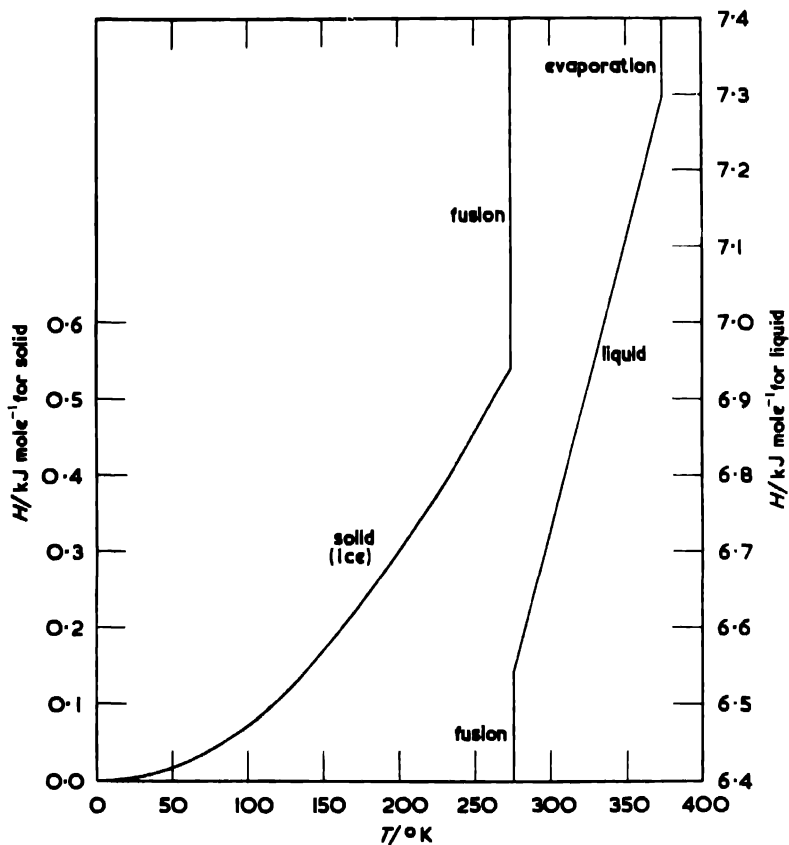
Fig. 4. 1. Heat function of H_2O at one atmosphere

Suppose we wish to know by how much the entropy of steam at 1000 °K and 1 atmosphere exceeds the entropy of ice at 0 °K. We have to add the following contributions.

(a)   Ice at 0 °K → ice at 273.15 °K

   $\Delta S = 38.09 \text{ J deg}^{-1} \text{ mole}^{-1}$ (area under ice curve)

(b)   Ice at 273.15 °K → liquid water at 273.15 °K

$$\Delta S = \frac{\Delta H}{T} = \frac{6007 \text{ J mole}^{-1}}{273.15 \text{ deg}} = 21.99 \text{ J deg}^{-1} \text{ mole}^{-1}$$

(c)   Water at 273.15 °K → water at 373.15 °K

$\Delta S = 23.52 \text{ J deg}^{-1} \text{ mole}^{-1}$ (area under water curve)
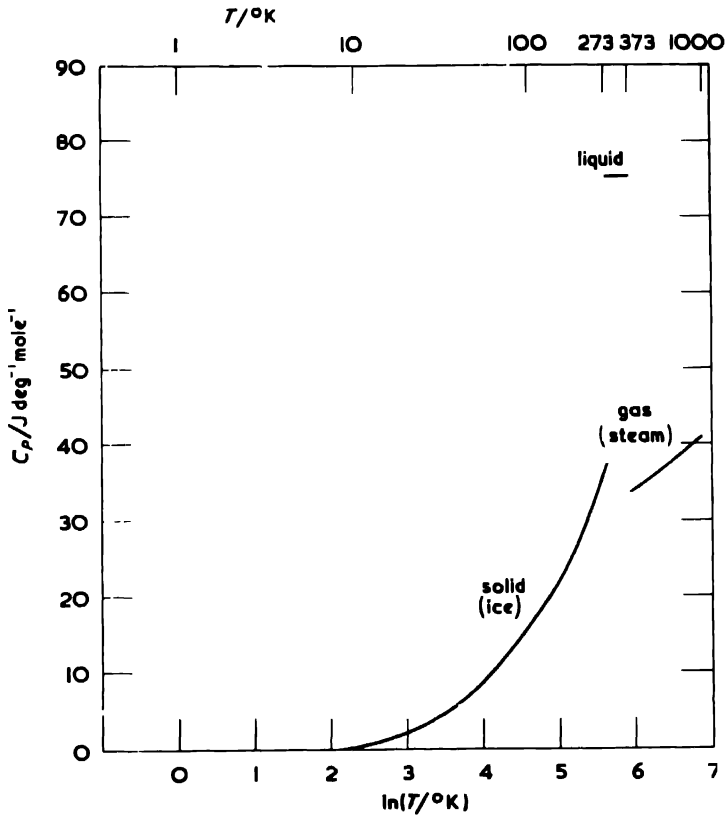
Fig. 4. 2. Heat capacity of H_2O at one atmosphere

(d)   Water at 373.15 °K → steam at 373.15 °K

$$\Delta S = \frac{\Delta H}{T} = \frac{40656 \text{ J mole}^{-1}}{373.15 \text{ deg}} = 108.95 \text{ J deg}^{-1} \text{ mole}^{-1}$$

(e)   Steam at 373.15 °K → steam at 1000 °K

$\Delta S = 35.8 \text{ J deg}^{-1} \text{ mole}^{-1}$ (area under steam curve)

By addition we obtain for the change

Ice at 0 °K → steam at 1000 °K   (at 1 atm.)

$$\Delta S = 228.4 \text{ J deg}^{-1} \text{ mole}^{-1}$$

In the case of some substances there may be several solid phases with transition temperatures at which the entropy increase ΔS is equal to the increase ΔH divided by T, but such transitions cause no difficulty.

We see then that the determination of changes in the entropy of any single substance through any range of temperature at constant pressure becomes straightforward provided the heat input and absolute temperature can be measured.

§ 4. 05 HEAT CAPACITY AT CONSTANT PRESSURE

In the previous section we saw that the determination of entropy requires us to use the relation

$$T \left(\frac{\partial S}{\partial T} \right)_P = \left(\frac{\partial H}{\partial T} \right)_P \qquad 4.\ 05.\ 1$$

This quantity is called the *heat capacity at constant pressure* of the system. If referred to one mole of substance this is called the *molar heat capacity at constant pressure* and will be denoted by C, or by C_P when it is desired to emphasize the contrast with another quantity C_V defined in § 4. 08. Thus using the subscript $_m$ to denote *molar* quantities

$$C = C_P = T \left(\frac{\partial S_m}{\partial T} \right)_P = \left(\frac{\partial H_m}{\partial T} \right)_P \qquad 4.\ 05.\ 2$$

The real importance of C is that it forms the connecting link between S and H. One measures directly H as a function of T and then determines S by the relation (1). Importance was in the past attached to C for a completely different, accidental and inadequate reason, namely that for many substances at the most usual temperatures C happens to be insensitive to the temperature. For example we notice from fig. 4. 2 that C is nearly constant for liquid water, only roughly constant for steam, but not at all constant for ice.

§ 4. 06 SO-CALLED MECHANICAL EQUIVALENT OF HEAT

Before the classical experiments of Joule, the relationship between work, heat and energy was not understood. These experiments established that within the experimental error the work or energy input

required to raise the temperature of a given mass of water through a given temperature range is independent of the particular mechanism used. The formulation of the first principle of thermodynamics is largely based on these experiments and later repetitions and improvements of them. Since Joule's experiments were performed before the formulation of the first principle, Joule's terminology was necessarily different from the terminology based on familiarity with the principles of thermodynamics. Joule described some of his experiments as the "determination of the mechanical equivalent of heat". Once the principles of thermodynamics are understood, this phrase becomes meaningless. What Joule in fact did was

(a) to establish an experimental basis for the formulation of the first principle of thermodynamics;

(b) to measure the *heat capacity of water*.

Before the first principle of thermodynamics was formulated or understood the unit of heat was the quantity of heat required to raise the temperature of one gram of water by one degree centigrade and this unit was called the *calorie*. Work was however measured in mechanical units. It is found that the heat capacity of liquid water is approximately $4.18 \, J \, deg^{-1} \, g^{-1}$ but in fact varies appreciably with the temperature. Nowadays almost all accurate thermal experiments involve measurements of volts, amperes and seconds leading to energy values in joules. Moreover the International Union of Physics in 1948 recommended * that all accurate calorimetric data should be expressed in joules. It is difficult to understand why the use of the calorie as a unit persists, except as a habit. The most careful experimental workers have in fact abandoned the old definition of the calorie and have replaced it by the more satisfactory definition †

$$1 \text{ calorie} = 4.1840 \text{ joules}$$

The calorie thus defined is called the *thermochemical calorie.*

As already mentioned the heat capacity of liquid water is approximately, but by no means exactly, independent of the temperature. Its value is very near $1 \, cal \, deg^{-1} \, g^{-1}$ at 290 °K. The best experimental values at a few other temperatures are as follows: †

* *International Union of Physics, Document* SG 48—6.

† See Stille, *Messen und Rechnen in der Physik* 1955.

At   0 °C 4.2174 J deg^{-1} g^{-1}
15 °C 4.1855 ,,   ,,   ,,
16 °C 4.1846 ,,   ,,   ,,
17 °C 4.1837 ,,   ,,   ,,
20 °C 4.1816 ,,   ,,   ,,
25 °C 4.1793 ,,   ,,   ,,

§ 4. 07 DEPENDENCE OF ENTROPY ON PRESSURE

In § 4. 04 we saw how the variation of entropy with the temperature at a constant pressure is determined experimentally. In order to determine the entropy as a function of temperature and pressure, this procedure has to be supplemented by a determination of the dependence of entropy on pressure at constant temperature. This dependence is given according to Maxwell's relation (3. 04. 4) by

$$\left(\frac{\partial S}{\partial P}\right)_T = -aV \qquad 4.\ 07.\ 1$$

which integrated becomes

$$S\left(T, P^{II}\right) - S\left(T, P^{I}\right) = -\int_{P^I}^{P^{II}} aV \mathrm{d}P \qquad 4.\ 07.\ 2$$

If we differentiate (1) with respect to T, keeping P constant, and multiply by T we obtain

$$\left(\frac{\partial C}{\partial P}\right)_T = -T\left\{\frac{\partial\,(aV)}{\partial T}\right\}_P = -a^2 TV - T\left(\frac{\partial a}{\partial T}\right)_P V \qquad 4.\ 07.\ 3$$

The second term on the right will usually be small compared with the first for solids and liquids; for gases on the contrary the two terms are nearly equal and opposite.

§ 4. 08 HEAT CAPACITY AT CONSTANT VOLUME

In §§ 4. 04—4. 07 we have collected the most important formulae required to determine the entropy in terms of temperature and pressure. There is an analogous set of relations for the alternative choice of temperature and volume as independent variables. Except for gases these relations are considerably less used than those relating to the independent variables T, P. We shall refer to them quite briefly, without giving detailed derivations; these are in all cases analogous to those in the T, P system.

For the dependence of entropy on temperature at constant volume, we have

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V \qquad 4.\,08.\,1$$

which integrated becomes

$$S\,(T_2,\,V) - S\,(T_1,\,V) = \int_{T_1}^{T_2}\left(\frac{\partial U}{\partial T}\right)_V \frac{\mathrm{d}T}{T} \qquad 4.\,08.\,2$$

Correspondingly for the dependence of entropy on volume at constant temperature, we have according to Maxwell's relation (3. 04. 3)

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{a}{\varkappa} \qquad 4.\,08.\,3$$

which integrated becomes

$$S\,(T,\,V^{II}) - S\,(T,\,V^I) = \int_{V^I}^{V^{II}} \frac{a}{\varkappa}\,\mathrm{d}V \qquad 4.\,08.\,4$$

The quantity $(\partial U/\partial T)_V$ in formula (1) is called the *heat capacity at constant volume* of the system. The corresponding quantity referred to one mole is called the *molar heat capacity at constant volume* and is denoted by C_V. Thus

$$C_V = T\left(\frac{\partial S_m}{\partial T}\right)_V = \left(\frac{\partial U_m}{\partial T}\right)_V \qquad 4.\,08.\,5$$

§ 4. 09 RELATION BETWEEN HEAT CAPACITIES

If in the general relation (3. 01. 23) we substitute S for w, T for x, P for y and V for z we find

$$\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_F \qquad 4.\,09.\,1$$

Substituting from (3. 03. 2) and from Maxwell's relation (3. 04. 3) into (1), we obtain

$$\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_V + \frac{a^2 V}{\varkappa} \qquad 4.\,09.\,2$$

Applying (2) to one mole, multiplying by T and using the definitions (4. 05. 2) and (4. 08. 5) of C_P and C_V respectively we find

$$C_P = C_V + \frac{a^2 T V_m}{\varkappa} \qquad 4.\,09.\,3$$

Since in a stable phase none of the quantities α^2, T, V_m, $\varkappa$ can ever be negative, it follows that C_P can never be less than C_V.

C_V is much more difficult to measure than C_P. If the value of C_V is required, it is usual to measure C_P and then calculate C_V from (3). C_V is altogether less important than C_P. There seems to be a widespread belief that in the comparison of a theoretical model with experimental data the most suitable quantity for the comparison is C_V. This is however a misconception. Any theoretical model susceptible to explicit analytical treatment, such as for example Debye's model of a crystal, discussed in § 4. 37, leads to an explicit formula for the free energy and so by differentiation with respect to T to explicit formulae for the energy and the entropy, both of which are directly measurable as a function of temperature. These are clearly the most suitable quantities for comparison between a theoretical model and experimental data. There is no reason or excuse for a further differentiation to obtain a heat capacity except in the case that the agreement between theory and experiment is so good that a more sensitive test is required. This may in fact be the case for some gases, but it is certainly not the case for solids or liquids.

§ 4. 10 CONDENSED PHASES AND GASES

Solids and liquids, which we shall class together under the name *condensed phases*, are under most conditions sharply distinguished from gases by a striking difference in compressibility. It is true that in the neighbourhood of the critical point, as we shall see in § 4. 48, the distinction between liquid and gas disappears, but at least for liquids or solids at temperatures well below the critical temperature and for gases at pressures well below the critical pressure the contrast is striking.

In a condensed phase at a given temperature the compressibility is small and practically independent of the pressure. That is to say that to a first approximation the volume is independent of the pressure and to a better approximation decreases linearly with the pressure. In a gas on the other hand the compressibility is much greater and far from independent of the pressure. In fact it is at least roughly true that the volume of a gas varies inversely as the pressure, according to *Boyle's Law*. In other words it is PV, not V, which to a first approximation is independent of P.

§ 4. 11 ISOTHERMAL BEHAVIOUR OF A GAS

It is reasonable to expect that the volume of any phase at constant temperature can be expressed as a power series in the pressure. In view

of what was said in the previous section, the leading term will in the case of a gas be an inverse first power. We may accordingly write

$$V = \frac{A}{P} + B + C'P + \ldots \qquad \qquad 4.11.1$$

In principle the number of terms is indefinite, depending on the accuracy aimed at. Up to quite high pressures, of say a hundred atmospheres, it is usually unnecessary to use terms beyond $C'P$. At pressures up to a few atmospheres even this term is usually negligible, only the terms A/P and B being required. All the coefficients A, B, C', ... of course depend on the temperature, but not on the pressure.

In the treatment of gases it is sometimes convenient to regard T, V rather than T, P as independent variables. We then express the pressure as a power series in the density or in the reciprocal of the volume. We accordingly write

$$P = \frac{A}{V}\left\{ 1 + \frac{B}{V} + \frac{C}{V^2} + \ldots \right\} \qquad \qquad 4.11.2$$

The coefficients A and B are common to the two formulae (1) and (2); C and C' are connected by

$$C = B^2 + AC' \qquad \qquad 4.11.3$$

There are more complicated relations between any higher coefficients which may be included.

B is called the *second virial coefficient*; C is called the *third virial coefficient* and so on.

It is mainly a question of convenience or taste whether one uses a formula of type (1) or of type (2). For our immediate purpose, it is more convenient to use (1). Fortunately at ordinary pressures all terms beyond the second are usually negligible and either formula then reduces to

$$V = \frac{A}{P} + B \qquad \text{(low pressures)} \qquad \qquad 4.11.4$$

From (1) we readily obtain the Gibbs function G as a function of pressure by substituting into (3.05.1) and integrating. We thus find

$$G(T, P) - G(T, P\dagger) = A \ln \frac{P}{P\dagger} + B(P - P\dagger) + \tfrac{1}{2}C'(P^2 - P\dagger^2) \quad 4.11.5$$

where $P\dagger$ is an arbitrarily chosen standard pressure.

We obtain for the heat function H by substituting (5) into (3. 06. 3)

$$H\left(T, P\right) - H\left(T, P^\dagger\right) = \left(A - T\frac{dA}{dT}\right)\ln\frac{P}{P^\dagger}$$

$$+ \left(B - T\frac{dB}{dT}\right)(P - P^\dagger) + \frac{1}{2}\left(C' - T\frac{dC'}{dT}\right)(P^2 - P^{\dagger 2}) \qquad 4.\,11.\,6$$

§ 4. 12 THROTTLING EXPERIMENT

In the previous section we set up a formula for V as a function of P based on experiment. From this we deduced a formula for G and thence a formula for H. We shall now consider the comparison between this formula for H and experiment.

The experiment which supplies the most direct information concerning the dependence of H on the pressure at constant temperature is known as *throttling*. The first experiment of this type was performed by Joule and Lord Kelvin (William Thomson); it is accordingly often called the *Joule-Thomson experiment*. In this experiment a stream of gas in a thermally insulated container is forced through a plug, the pressure being greater on the near side than on the far side and the temperatures of the gas stream approaching and leaving the plug are measured on an arbitrary scale; we denote the temperatures on this scale by θ to distinguish them sharply from absolute temperatures T, which we do not yet know how to measure. Consider now the whole system in a steady state such that in a given time a certain mass of gas is pushed in at a pressure P_1 and during the same time an equal mass of gas streams away at a pressure P_2. We use the subscript 1 to denote the state of the gas being pushed in and the subscript 2 to denote that of the gas streaming away. Then during the time considered a mass of gas of pressure P_2, volume V_2, temperature θ_2 and energy U_2 is displaced by an equal mass of pressure P_1, volume V_1, temperature θ_1 and energy U_1. During this time the work done on the system is $P_1V_1 - P_2V_2$. Since the system is supposed thermally insulated this work must be equal to the increase in energy of the system. Thus

$$U_2 - U_1 = P_1V_1 - P_2V_2 \qquad 4.\,12.\,1$$

Hence according to the definition (1. 31. 2) of H, we have

$$H_2 = H_1 \qquad 4.\,12.\,2$$

or choosing θ, P as independent variables

$$H\left(\theta_1, P_1\right) = H\left(\theta_2, P_2\right) \qquad 4.\,12.\,3$$

Suppose that the effect of throttling is to cool the gas, so that θ_2 is a lower temperature than θ_1, then there is no difficulty in principle in heating the throttled gas at constant pressure so as to restore its temperature from θ_2 to θ_1. If the heat required for this purpose is measured, we then know the value of

$$H(\theta_1, P_2) - H(\theta_2, P_2) \qquad 4.12.4$$

which according to (3) is equal to

$$H(\theta_1, P_2) - H(\theta_1, P_1) \qquad 4.12.5$$

If on the contrary the effect of throttling is to warm the gas, then we must do a subsidiary experiment to determine the heat required to raise the temperature of the gas at the pressure P_2 from θ_1 to θ_2. We thus obtain an experimental value of

$$H(\theta_2, P_2) - H(\theta_1, P_2) \qquad 4.12.6$$

which according to (3) is equal to

$$H(\theta_1, P_1) - H(\theta_1, P_2) \qquad 4.12.7$$

In either case we obtain experimental values of $H(\theta_1, P_2) - H(\theta_1, P_1)$ positive in the former case, negative in the latter. It is important to notice that this experiment does not require any knowledge of how the arbitrary θ scale of temperature is related to the absolute scale or to any other scale.

We shall now describe the experimental results obtained. It is found that, whatever the temperature, $H(P_1) - H(P_2)$ is at least approximately proportional to $P_1 - P_2$ and not very sensitive to the absolute magnitude of P_1. It is quite certain that at very low values of P_2, the value of $H(P_1) - H(P_2)$ does not tend towards infinity, which is what one should expect from formula (4.11.6) owing to the term in $\ln P$. In short the Joule-Thomson experiment shows that the first term on the right of formula (4.11.6) is in fact missing and the linear term in P is therefore the leading one.

§ 4.13 MEASUREMENT OF ABSOLUTE TEMPERATURE

In principle to determine T, one should measure ΔH and ΔG for the same isothermal process and by comparing these obtain a differential equation for T. In particular, one can determine the coefficients A, B, C' in the formula for G simply by pressure measurements and one can obtain independent measurements of $(A - TdA/dT)$, $(B - TdB/dT)$, $(C' - TdC'/dT)$ the coefficients in H, from the throttling experiment.

By comparison we obtain information concerning T, but admittedly in a rather awkward form.

To our agreeable surprise the information is in a strikingly convenient form in the case of the coefficient A. The Joule-Thomson experiment shows unmistakably that H contains no term tending to infinity as P tends to zero, that is to say no term in $\ln P$. Hence from (4. 11. 6) we conclude that

$$A - T\frac{\mathrm{d}A}{\mathrm{d}T} = 0 \qquad \text{4. 13. 1}$$

which is equivalent to

$$A \propto T \qquad \text{4. 13.}$$

At last we have found a simple, direct and reliable way of determining the ratio of any two absolute temperatures. We use as a thermometer a fixed quantity of gas. We measure several pairs of values of P, V at the same temperature and extrapolate the product PV to $P = 0$, thus obtaining the value of A. We repeat this at another temperature thus obtaining another value of A. Then the ratio of these two values of A is equal to the ratio of the two values of T. Having thus established a way of determining the ratio of any two temperatures, the numerical values are fixed by the convention described in § 1. 18 so that the triple point of water is 273.16 degrees and this is called the Kelvin scale.

§ 4. 14 THE GAS CONSTANT AND THE MOLE. EQUATION OF STATE OF GAS

We have found that the coefficient A is directly proportional to the temperature. Since the volume is an extensive quantity, it is obvious that A is also an extensive quantity proportional to the quantity of gas to which it applies. We accordingly write

$$A = nRT \qquad \text{4. 14. 1}$$

where n denotes the number of units of quantity and R is independent of temperature, pressure and quantity of gas. R also becomes independent of the nature of the gas when the unit of quantity is suitably chosen, e.g. by choosing the *mole*. From a purely thermodynamic view-point the *mole* is defined without any reference to molecular theory as follows. The mole of any substance is that quantity which has the same value of R as 32 grams of oxygen gas. This value is

$$
\begin{aligned}
R &= 8.3147 \text{ J deg}^{-1} \text{mole}^{-1} \\
&= 8.3147 \times 10^7 \text{ erg deg}^{-1} \text{mole}^{-1} \\
&= 1.98726 \text{ cal deg}^{-1} \text{mole}^{-1} \\
&= 0.082057 \text{ atm l deg}^{-1} \text{mole}^{-1} \qquad \text{4. 14. 2}
\end{aligned}
$$

When the mole is defined in this manner, then it can be shown by statistical mechanics or kinetic theory that the number of molecules in a mole is the same for every gas. This number is called *Avogadro's number*. It is defined as the number of atoms of oxygen in 16 grams and is denoted by L. Its value is

$$L = 0.6024 \times 10^{24} \text{ mole}^{-1} \qquad 4.\,14.\,3$$

The gas constant R is related to Boltzmann's constant k introduced in chapter 2 by

$$R = Lk \qquad 4.\,14.\,4$$

We now consider formula (4. 11. 1) applied to one mole of a gas and we accordingly replace A by RT. We thus obtain

$$V_m = \frac{RT}{P} + B + C'P \qquad 4.\,14.\,5$$

This is called the *equation of state* of a gas. Under ordinary conditions the term in $C'P$ is negligible and for the sake of brevity we shall omit it. If it is required, it should be obvious how to insert it into the formulae. We accordingly replace (5) by

$$V_r = \frac{RT}{P} + B\,(T) \qquad 4.\,14.\,6$$

It is clear that B has the dimensions of a volume per unit quantity and is a function of temperature only.

§ 4. 15 ABSOLUTE ACTIVITY

In chapter 2 we met a quantity called the absolute activity which plays an important part in the statistical thermodynamics of open systems. It is related to the molecular chemical potential μ by $\lambda = e^{\mu/kT}$. We now give a purely thermodynamic definition of the absolute activity which is somewhat out of place in the present chapter, but we could not give it earlier because it involves the gas constant R. We accordingly define * the *absolute activity* as related to the molar chemical potential μ by

$$\lambda = e^{\mu/RT} \qquad 4.\,15.\,1$$

or

$$\mu = RT \ln \lambda \qquad 4.\,15.\,2$$

Whereas it is not necessary to use λ as well as μ, we shall find that the absolute activity λ is often a convenient function in the study

* See Fowler and Guggenheim, *Statistical Thermodynamics* 1939 p. 66.

of equilibria of all kinds whether involving one species or several. In § 1. 49 we showed that for the most general chemical reaction represented symbolically by

$$\Sigma \nu_A A \rightarrow \Sigma \nu_B B \qquad \text{4. 15. 3}$$

the condition for equilibrium is according to (1. 49. 9)

$$\Sigma \nu_A \mu_A = \Sigma \nu_B \mu_B \qquad \text{4. 15. 4}$$

We now see that this condition can equally be expressed in terms of absolute activities in the form

$$\Pi (\lambda_A)^{\nu_A} = \Pi (\lambda_B)^{\nu_B} \qquad \text{4. 15. 5}$$

or

$$\frac{\Pi (\lambda_B)^{\nu_B}}{\Pi (\lambda_A)^{\nu_A}} = 1 \qquad \text{4. 15. 6}$$

where the denominator is the product of the absolute activities of all the species on the left in the process (3) and the numerator is the product of the absolute activities of those on the right.

In particular the condition for the equilibrium distribution of a species i between the phases α and β may be written

$$\lambda_i^\alpha = \lambda_i^\beta \qquad \text{4. 15. 7}$$

We may note that the fundamental equations (1. 33. 12), (1. 33. 13) and (1. 33. 14) can be written

$$\frac{dS}{R} = \frac{1}{RT} dU + \frac{P}{RT} dV - \Sigma_i \ln \lambda_i \, dn_i \qquad \text{4. 15. 8}$$

$$\frac{dJ}{R} = \frac{U}{RT^2} dT + \frac{P}{RT} dV - \Sigma_i \ln \lambda_i \, dn_i \qquad \text{4. 15. 9}$$

$$\frac{dY}{R} = \frac{H}{RT^2} dT - \frac{V}{RT} dP - \Sigma_i \ln \lambda_i \, dn_i \qquad \text{4. 15. 10}$$

§ 4. 16 THERMODYNAMIC FUNCTIONS OF A GAS

In § 4. 11 we derived various thermodynamic functions from (4. 11. 1) Proceeding alternatively from (4. 14. 6) we obtain

$$\mu = \frac{G}{n} = G_m = \mu (P^\dagger) + RT \ln \frac{P}{P^\dagger} + BP - BP^\dagger \qquad \text{4. 16. 1}$$

where $P^\dagger$ is an arbitrarily chosen standard pressure, usually one atmosphere. We may write (1) in the alternative form

$$\mu = \frac{G}{n} = G_m = \mu^\dagger + RT \ln \frac{P}{P^\dagger} + BP \qquad 4.\,16.\,2$$

where $\mu^\dagger$ is a function of the temperature only. $\mu^\dagger$ is not exactly equal to the value of μ when the pressure is $P^\dagger$ but differs from it by $BP^\dagger$. The value of $\mu^\dagger$ depends of course on the choice of the standard pressure $P^\dagger$, but is independent of the units in which P and $P^\dagger$ are measured.

From (2) we derive immediately

$$S_m = \frac{S}{n} = -\frac{\mathrm{d}\mu^\dagger}{\mathrm{d}T} - R \ln \frac{P}{P^\dagger} - P \frac{\mathrm{d}B}{\mathrm{d}T} \qquad 4.\,16.\,3$$

$$H_m = \frac{H}{n} = \mu^\dagger - T \frac{\mathrm{d}\mu^\dagger}{\mathrm{d}T} + \left(B - T \frac{\mathrm{d}B}{\mathrm{d}T}\right) P \qquad 4.\,16.\,4$$

$\mu^\dagger$ is called the *standard chemical potential*, $-\mathrm{d}\mu^\dagger/\mathrm{d}T$ the *standard molar entropy* and $\mu^\dagger - T\mathrm{d}\mu^\dagger/\mathrm{d}T$ the *standard molar heat function*. In general there does not exist any state in which the chemical potential, the molar entropy and the molar heat function are simultaneously equal to their standard values. We accordingly avoid the use of any expression such as "entropy in the standard state".

The compressibility $\varkappa$ is according to (4. 14. 6) given by

$$\varkappa = -\frac{1}{V_m}\left(\frac{\partial V_m}{\partial P}\right)_T = \frac{1}{P}\left(1 + \frac{PB}{RT}\right)^{-1} \qquad 4.\,16.\,5$$

and the coefficient of thermal expansion a by

$$aV_m = \left(\frac{\partial V_m}{\partial T}\right)_P = \frac{R}{P} + \frac{\mathrm{d}B}{\mathrm{d}T} \qquad 4.\,16.\,6$$

The molar heat capacity at constant pressure is given by

$$C = T\left(\frac{\partial S_m}{\partial T}\right)_P = \left(\frac{\partial H_m}{\partial T}\right)_P = -T \frac{\mathrm{d}^2\mu^\dagger}{\mathrm{d}T^2} - TP \frac{\mathrm{d}^2B}{\mathrm{d}T^2} \qquad 4.\,16.\,7$$

or

$$C = C^\dagger - TP \frac{\mathrm{d}^2B}{\mathrm{d}T^2} \qquad 4.\,16.\,8$$

where $C^\dagger$ denotes the limiting value of C at zero pressure.

From (2) and (4. 15. 1) we obtain for the absolute activity

$$\lambda = \lambda^\dagger \frac{P}{P^\dagger} e^{BP/RT} \qquad \text{4. 16. 9}$$

where

$$\lambda^\dagger = e^{\mu^\dagger/RT} \qquad \text{4. 16. 10}$$

is a function of the temperature only.

§ 4. 17 JOULE-THOMSON COEFFICIENT

When we discussed the throttling experiment in § 4. 12, we stressed the fact that at that stage we could not yet measure the absolute temperature. Now that we know how to do this by means of a gas thermometer, it is profitable to return to a discussion of throttling. The conditions of the gas before and after throttling are related by

$$H(T_2, P_2) = H(T_1, P_1) \qquad \text{4. 17. 1}$$

Provided the pressure drop is not too great, we may usefully replace this by the differential relation

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = 0 \qquad \text{4. 17. 2}$$

The Joule-Thomson coefficient, which measures the ratio of the *temperature fall* to the *pressure drop*, is then

$$\frac{\partial T}{\partial P}\bigg)_H = -\left(\frac{\partial H}{\partial P}\right)_T \bigg/ \left(\frac{\partial H}{\partial T}\right)_P = -\left(\frac{\partial H_m}{\partial P}\right)_T \bigg/ \left(\frac{\partial H_m}{\partial T}\right)_P \qquad \text{4. 17. 3}$$

By substitution from (3. 05. 4) and (4. 05. 2), this becomes

$$\frac{\partial T}{\partial P}\bigg)_H = \frac{-V_m(1 - aT)}{C_P} \qquad \text{4. 17. 4}$$

where we have written C_P rather than C to avoid possible confusion with the third virial coefficient.

If we assume the equation of state (4. 14. 6) then a is given by (4. 16. 6). Substituting this value of a into (4) we obtain for the Joule-Thomson coefficient

$$\frac{\partial T}{\partial P}\bigg)_H = \frac{-B + T\dfrac{dB}{dT}}{C_P} = \frac{T^2}{C_P}\frac{d(B/T)}{dT} \qquad \text{4. 17. 5}$$

§ 4. 18 DEPENDENCE OF SECOND VIRIAL COEFFICIENT ON TEMPERATURE

The second virial coefficient B is negative at low temperatures, but increases with the temperature and eventually becomes positive.

It is customary to measure B for each gas in a unit of volume equal to that at 0 °C and a pressure of one atmosphere. This is called the

TABLE 4. 1

Second virial coefficient of nitrogen.

$T/°K$	$10^4 B/$Amagat units	B/cm^3 mole^{-1}
143	—35.6	—79.7
173	—23 1	—51.7
223	—11 8	—26.4
273	— 4.61	—10.3
323	— 0.11	— 0.2
373	2.74	6.1
423	5.14	11.5
473	6.85	15.3
573	9 21	20.6
673	10.5	23 5

Amagat unit of volume. It varies slightly from one gas to another according to the value of B but is always near to 22.4 1 mole^{-1}.

As a typical example of the way B depends on the temperature, we give in table 4. 1 some experimental values * for nitrogen. This dependence on temperature is shown in fig. 4. 3. The continuous curve through the experimental points has the empirical formula

$$\frac{B}{cm^3 \text{ mole}^{-1}} = 39.5 - \frac{1.00 \times 10^4 \text{ deg}}{T} - \frac{1.084 \times 10^6 \text{ deg}^2}{T^2} \qquad 4.\,18.\,1$$

It is not possible to fit the experimental points by any simpler formula. An attempt to obtain a fit by the formula

$$\frac{B}{cm^3 \text{ mole}^{-1}} = 22.6 \quad \frac{2.15 \times 10^6 \text{ deg}^2}{T^2} \qquad 4.\,18.\,2$$

known as Berthelot's equation is shown by the dotted curve. It is evident that a fit by this formula, or other formulae of the same type, can be obtained only over a short range of temperature.

* Holborn and Otto, *Z. Phys.* 1925 **33** 5. These authors' unit of B was not the Amagat unit but was the volume occupied by one mole at 0 °C and at a pressure of 1 m Hg.

§ 4. 19 BOYLE TEMPERATURE AND INVERSION TEMPERATURE

At the temperature T_B at which B changes sign, Boyle's Law $PV_m = RT_B$ is accurate for low pressures and this temperature T_B is accordingly called the *Boyle temperature*. For nitrogen according to (4. 18. 1) the Boyle temperature is 335 °K.

According to the way B depends on the temperature the Joule-Thomson coefficient is positive at the lowest temperatures (cooling by throttling) but is negative at higher temperatures (heating by throttling). The temperature T_i at which the effect changes sign is called the *inversion temperature*. According to (4. 17. 5) the inversion temperature is determined by

$$\frac{\mathrm{d}B}{\mathrm{d}T} \quad \frac{B}{T} \qquad\qquad 4.\,19.\,1$$

If B is plotted against T, then the tangent through the origin touches the curve at $T = T_i$. For nitrogen this is shown in fig. 4. 3.
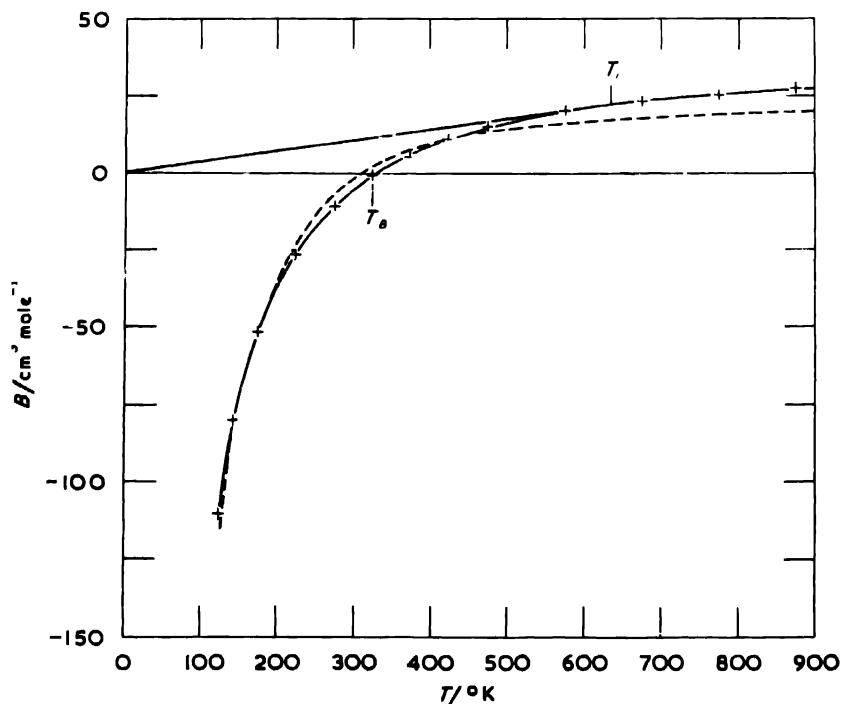
Fig. 4. 3 ———— formula (4.18.1) - - - - formula (4.18 2) (Berthelot)

§ 4. 20 VAN DER WAALS' EQUATION

In 1873 van der Waals suggested the formula

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT \qquad (a, b \text{ constant}) \qquad 4.\ 20.\ 1$$

as the equation of state for a gas with a, b constants characteristic of the gas. This equation gives a qualitative description of the behaviour of gases and also of liquids (see § 4. 52), and it has the one merit of simplicity. It is far from accurate and has no sound theoretical basis except for low pressures and high temperatures. At low pressures formula (1) is, apart from second order small quantities, equivalent to

$$V_m = \frac{RT}{P} + b - \frac{a}{RT} \qquad 4.\ 20.\ 2$$

According to the definition of the second virial coefficient B, formula (2) is equivalent to

$$B = b - \frac{a}{RT} \qquad 4.\ 20.\ 3$$

The actual temperature dependence of B is typified by that of nitrogen shown in fig. 4. 3. It has already been mentioned that the measurements cannot be accurately fitted by a formula as simple as

$$B = b - \frac{\iota}{T^2} \qquad 4.\ 20.\ 4$$

An attempt to obtain a fit by a formula of type (3) would be still less successful except at high temperatures.

§ 4. 21 PERFECT GAS

For many purposes, especially at low pressures, it is allowable to neglect the second and a fortiori the higher virial coefficients. The thermodynamic formulae of a gas then reduce to particularly simple forms, which are called the *formulae of a perfect gas*. It must be emphasized that there is no such thing as a perfect gas, which is an abstraction to which any real gas approximates more or less according to the nature of the gas and the conditions. From a molecular point of view the perfect gas laws correspond to the idealized behaviour of a system of molecules whose mutual interactions are neglected.

The most important formulae of a perfect gas are obtained directly from § 4. 14 and § 4. 16 by omitting all terms containing B.

We thus obtain

$$\mu = G_m = \frac{G}{n} = \mu^\dagger + RT \ln \frac{P}{P^\dagger} \qquad 4.\,21.\,1$$

$$S_m = \frac{S}{n} = -\frac{d\mu^\dagger}{dT} - R \ln \frac{P}{P^\dagger} \qquad 4.\,21.\,2$$

$$H_m = \frac{H}{n} = \mu^\dagger - T \frac{d\mu^\dagger}{dT} \qquad 4.\,21.\,3$$

$$V_m = \left(\frac{\partial \mu}{\partial P}\right)_T = \frac{RT}{P} \qquad 4.\,21.\,4$$

It will be observed that for a perfect gas the molar heat function H_m is independent of the pressure; this is merely another way of saying that B is ignored.

We have further

$$\varkappa = -\frac{1}{V_m}\left(\frac{\partial V_m}{\partial P}\right)_T = P^{-1} \qquad 4.\,21.\,5$$

$$a = \frac{1}{V_m}\left(\frac{\partial V_m}{\partial T}\right)_P = T^{-1} \qquad 4.\,21.\,6$$

$$C = T\left(\frac{\partial S_m}{\partial T}\right)_P = \frac{dH_m}{dT} = -T \frac{d^2\mu^\dagger}{dT^2} \qquad 4.\,21.\,7$$

$$\frac{\lambda}{\lambda^\dagger} = \frac{P}{P^\dagger} \qquad 4.\,21.\,8$$

We note that for a perfect gas C is independent of the pressure, but not independent of the temperature.

§ 4. 22 FUGACITY

Some of the formulae for real gases can be transcribed to forms having a simplicity resembling that of the formulae of perfect gases by the device due to G. N. Lewis [*] of introducing a fictitious pressure called the *fugacity*. We accordingly define the fugacity p^* by the two properties

$$p^* = \text{const.} \qquad (T \text{ const.}) \qquad 4.\,22.\,1$$

$$\frac{p^*}{P} \to 1 \text{ as } P \to 0 \qquad (T \text{ const.}) \qquad 4.\,22.\,2$$

[*] Lewis, *Proc. Nat. Acad. Sci., Wash.* 1901 **37** 49; *Z. phys. Chem.* 1901 **38** 205.

According to this definition, at low pressures the fugacity p^* is indistinguishable from the pressure P. At a given temperature as the pressure is increased so p^* deviates from P in such a manner that whereas the formula (4. 21. 8) becomes progressively less accurate formula (1) remains identically true.

From (4. 15. 2) and (1) we obtain

$$\mu = \mu\dagger + RT \ln \frac{p^*}{P\dagger} \qquad 4.\ 22.\ 3$$

From (3) all other thermodynamic functions can be derived, if required, by differentiation. For example

$$S_m = -\frac{d\mu\dagger}{dT} - R \ln \frac{p^*}{P\dagger} - RT \left(\frac{\partial \ln p^*}{\partial T}\right)_I \qquad 4.\ 22.\ 4$$

$$V_m = RT \left(\frac{\partial \ln p^*}{\partial P}\right)_T \qquad 4.\ 22.\ 5$$

The simplification attained by the introduction of the fugacity is one of appearance or elegance, but leads to nothing quantitative unless we express the fugacity in terms of the pressure and we are then back where we started. Thus at ordinary pressures when we may neglect all virial coefficients beyond the second, the absolute activity is given by (4. 16. 9). Comparing this with (1) and (2) we see that

$$p^* = Pe^{BP/RT} \qquad 4.\ 22.\ 6$$

or

$$\ln p^* = \ln P + \frac{BP}{RT} \qquad 4.\ 22.\ 7$$

When we substitute (7) into (3) and (4) we recover (4. 16. 2) and (4. 16. 3) respectively.

In general we can obtain a formula for p^* by integrating (5) adjusting the integration constant so as to satisfy (2). For example, at higher pressures where we have to use (4. 14. 5) instead of (4. 14. 6) we obtain

$$\ln p^* = \ln P + \frac{1}{RT}(BP + \tfrac{1}{2}C'P^2) \qquad 4.\ 22.\ 8$$

§ 4. 23 T, V FORMULAE FOR GASES

In our discussion of gases we have up to the present used the independent variables T, P and we accordingly started from formula (4. 14. 5), namely

$$V_m = \frac{RT}{P} + B + C'P \qquad\qquad 4.\,23.\,1$$

If however we prefer to use the independent variables T, V then we should start from the formula

$$P = \frac{RT}{V_m} \left\{ 1 + \frac{B}{V_m} + \frac{C}{V_m^2} \right. \qquad\qquad 4.\,23.\,2$$

which is equivalent to (1) apart from small quantities of a higher order involving the fourth virial coefficient. C and C' are related by

$$C = B^2 + RTC' \qquad\qquad 4.\,23.\,3$$

We shall actually neglect the terms containing C, just as we previously neglected terms containing C'. If they are required there is no difficulty in inserting them. We accordingly reduce (2) to

$$P = \frac{RT}{V_m} \left(1 + \frac{B}{V_m} \right) = \frac{nRT}{V} \left(1 + \frac{nB}{V} \right) \qquad\qquad 4.\,23.\,4$$

By integrating (4) with respect to V we obtain

$$F = nF_m = n\mu^\dagger - nRT + nRT \ln \frac{nRT}{P^\dagger V} + \frac{n^2 RTB}{V} \qquad\qquad 4.\,23.\,5$$

wherein the integration constant, a function of T, has been written in such a form as to be consistent with (4. 16. 2). This may be seen by differentiating (5) with respect to n when we obtain

$$\mu = \left(\frac{\partial F}{\partial n} \right)_{T,V} = \mu^\dagger + RT \ln \frac{RT}{P^\dagger V_m} + \frac{2RTB}{1} \qquad\qquad 4.\,23.\,6$$

which is equivalent to (4. 16. 2) apart from higher order small terms.

By differentiation of (5) with respect to T we obtain

$$S_m = \overset{\smile}{} = -\frac{d\mu}{dT} - R \ln \frac{RT}{P^\dagger V_n} - R \frac{B}{V_n} - \frac{RT}{V_m} \frac{dB}{dT} \qquad\qquad 4.\,23.\,7$$

and

$$U_m = \frac{U}{n} = \mu^\dagger - T \frac{d\mu^\dagger}{dT} - RT - \frac{RT^2}{V_m} \frac{dB}{dT} \qquad\qquad 4.\,23.\,8$$

By further differentiation of (7) or (8) with respect to T, we obtain

$$C_V = T\left(\frac{\partial S_m}{\partial T}\right)_{V,\,n} = \left(\frac{\partial U_m}{\partial T}\right)_{V,\,n}$$

$$= -T\frac{\mathrm{d}^2\mu^\dagger}{\mathrm{d}T^2} - R - \frac{R}{V_m}\frac{\mathrm{d}}{\mathrm{d}T}\left(T^2\frac{\mathrm{d}B}{\mathrm{d}T}\right) \qquad 4.\,23.\,9$$

§ 4. 24 RELATION BETWEEN C_P AND C_V FOR GASES

Neglecting all small quantities of higher orders than B/V_m, we may replace (4. 23. 9) by

$$C_V = -T\frac{\mathrm{d}^2\mu^\dagger}{\mathrm{d}T^2} - R - \frac{P}{T}\frac{\mathrm{d}}{\mathrm{d}T}\left(T^2\frac{\mathrm{d}B}{\mathrm{d}T}\right) \qquad 4.\,24.\,1$$

Subtracting this from (4. 16. 7) we obtain

$$C_P - C_V = R + 2P\frac{\mathrm{d}B}{\mathrm{d}T} \qquad 4.\,24.\,2$$

We shall now verify that (2) is consistent with the general thermo-dynamic relation (4. 09. 3) namely

$$C_P - C_V = a^2 T V_n \qquad 4.\,24.\,3$$

According to (4. 16. 6) we have

$$aV_m = \frac{R}{n}\left(1 + \frac{P}{R}\frac{\mathrm{d}B}{\mathrm{d}T}\right) \qquad 4.\,24.\,4$$

and according to (4. 16. 5)

$$\frac{1}{\varkappa} = P\left(1 + \frac{PB}{RT}\right) \qquad 4.\,24.\,5$$

while by definition of B we have

$$V_m = \frac{RT}{n}\left(1 + \frac{PB}{RT}\right) \qquad 4.\,24.\,6$$

Substituting (4), (5) and (6) into (3) we obtain, after some cancelling,

$$C_P - C_V = R\left(1 + \frac{P}{R}\frac{\mathrm{d}B}{\mathrm{d}T}\right)^2 \qquad 4.\,24.\,7$$

which agrees with (2) as far as the terms of order B/V_m.

§ 4. 25 T, V FORMULAE FOR PERFECT GASES

If in the formulae of the last two sections we omit all terms containing B, we obtain the corresponding simpler formulae for perfect gases. In particular

$$F_m = \frac{F}{n} = \mu^\dagger - RT + RT \ln \frac{RT}{P^\dagger V_m} \qquad 4.\,25.\,1$$

$$\mu = G_m = \mu^\dagger + RT \ln \frac{RT}{P^\dagger V_m} \qquad 4.\,25.\,2$$

$$P = \frac{RT}{V_m} \qquad 4.\,25.\,3$$

$$U_m = \frac{U}{n} = \mu^\dagger - T \frac{d\mu^\dagger}{dT} \quad RT \qquad 4.\,25.\,4$$

$$C_V = - T \frac{d^2\mu^\dagger}{dT^2} - R = C_P - R \qquad 4.\,25.\,5$$

We see from the formulae of § 4. 21 and the present section that for a perfect gas at a given temperature each of the following quantities is independent of pressure or volume: PV_m, H_m, U_m, C_P, C_V.

§ 4. 26 ADIABATIC COMPRESSIBILITY

In § 3. 03 the isothermal compressibility $\varkappa$ or $\varkappa_T$ was defined by

$$\varkappa_T = - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \qquad 4.\,26.\,1$$

The adiabatic compressibility $\varkappa_S$ is similarly defined by

$$\varkappa_S = - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right) \qquad 4.\,26.\,2$$

If in formula (3. 01. 14) we write V for x, P for y and S for z we obtain

$$\left(\frac{\partial V}{\partial P} \right)_S = - \left(\frac{\partial S}{\partial P} \right)_V \bigg/ \left(\frac{\partial S}{\partial V} \right)_P \qquad 4.\,26.\,3$$

whereas if we write V for x, P for y and T for z we obtain

$$\left(\frac{\partial V}{\partial P} \right)_T = - \left(\frac{\partial T}{\partial P} \right)_V \bigg/ \left(\frac{\partial T}{\partial V} \right)_P \qquad 4.\,26.\,4$$

Dividing (3) by (4) and comparing with (1), (2) we obtain

$$\frac{\varkappa_S}{\varkappa_T} = \frac{\left(\frac{\partial V}{\partial P}\right)_S}{\left(\frac{\partial V}{\partial P}\right)_T} = \frac{\left(\frac{\partial S}{\partial P}\right)_V}{\left(\frac{\partial T}{\partial P}\right)_V}\frac{\left(\frac{\partial T}{\partial V}\right)_P}{\left(\frac{\partial S}{\partial V}\right)_P} = \frac{\left(\frac{\partial S}{\partial T}\right)_V}{\left(\frac{\partial S}{\partial T}\right)_P} \qquad 4.\,26.\,5$$

using (3. 01. 24). According to the definitions (4. 05. 2) of C_P and (4. 08. 5) of C_V, (5) becomes

$$\frac{\varkappa_S}{\varkappa_T} = \frac{C_V}{C_P} \qquad 4.\,26.\,6$$

§ 4. 27 ADIABATIC EQUATIONS

For an adiabatic change we have by combining (4. 26. 2) with (4. 26. 6)

$$-\frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}P} = \frac{C_V}{C_P}\varkappa_T \qquad (S \text{ constant}) \qquad 4.\,27.\,1$$

This differential equation for an adiabatic change can not be integrated unless the right side can be expressed as an explicit function of P, V and not necessarily even then. In the special case of a perfect gas, according to (4. 21. 5) $\varkappa_T = P^{-1}$ and so (1) becomes

$$\frac{\mathrm{d}\ln V}{\mathrm{d}\ln P} = -\frac{C_V}{C_P} \qquad (S \text{ constant}) \qquad 4.\,27.\,2$$

We have seen that for a perfect gas C_P and C_V are constants at constant T but they are usually not constant at constant S (varying T). In the exceptional case of a perfect gas with monatomic molecules, we shall see in § 4. 29 that

$$C_V = \tfrac{3}{2}R \qquad C_P = \tfrac{5}{2}R \qquad \text{(monatomic molecules)} \qquad 4.\,27.\,3$$

so that (2) becomes

$$\frac{\mathrm{d}\ln V}{\mathrm{d}\ln P} = -\frac{3}{5} \qquad \text{(monatomic molecules)} \qquad 4.\,27.\,4$$

which can be integrated to

$$PV^{5/3} = \text{const.} \qquad \text{(monatomic molecules)} \qquad 4.\,27.\,5$$

Again for a perfect gas of diatomic molecules, we shall see in § 4. 30 that over a wide range of temperature

$$C_V = \tfrac{5}{2}R \qquad C_P = \tfrac{7}{2}R \qquad \text{(diatomic molecules)} \qquad 4.\,27.\,6$$

so that (2) becomes

$$\frac{\mathrm{d}\ln V}{\mathrm{d}\ln P} = -\frac{5}{7} \qquad \text{(diatomic molecules)} \qquad 4.\,27.\,7$$

which can be integrated to

$$PV^{7/5} = \text{const.} \qquad \text{(diatomic molecules)} \qquad 4.\,27.\,8$$

In other cases (2) cannot be integrated exactly.

§ 4. 28 TEMPERATURE DEPENDENCE OF $\mu^\dagger$ AND $\lambda^\dagger$

We have in § 4. 16 and § 4. 23 expressed all the most important thermodynamic functions in terms of $\mu^\dagger$ a function of temperature only, and we must now consider the form of $\mu^\dagger$.

In the first place $\mu^\dagger$ contains an arbitrary constant term, which we shall denote by H^0, depending only on the arbitrarily chosen zero of energy. Since H^0 is a constant, $\mathrm{d}H^0/\mathrm{d}T$ is zero and so by (4. 16. 4) the corresponding term in H_m is just H^0. This explains our choice of the notation H^0. According to (4. 23. 8) the corresponding term in U_m is $H^0 - RT$. According to (4. 16. 10) there is a corresponding arbitrary factor $e^{H^0/RT}$ in $\lambda^\dagger$.

Apart from the arbitrary constant in $\mu^\dagger$ and arbitrary factor in $\lambda^\dagger$, these quantities depend on the temperature in a manner determined by the nature of the gaseous molecules and it is convenient to divide these into four classes, namely

> monatomic molecules,
> diatomic molecules,
> polyatomic linear molecules,
> polyatomic non-linear molecules,

which we shall consider in turn.

§ 4. 29 MONATOMIC MOLECULES

For gases having monatomic molecules $\lambda^\dagger$ has the simple form given by

$$\lambda^\dagger = e^{H^0/RT}\left(\frac{\Theta^\dagger}{T}\right)^{\!\frac{5}{2}} \qquad 4.\,29.\,1$$

where $\Theta^\dagger$ is a constant, with the dimensions of temperature, depending

on the arbitrarily chosen standard pressure $P^\dagger$ and also on the arbitrarily chosen zero of entropy. We shall return to the more detailed consideration of $\Theta^\dagger$ in § 4. 56.

By substituting (1) into the formulae of § 4. 16 we derive

$$\mu^\dagger = H^0 - \tfrac{5}{2}RT \ln \frac{T}{\Theta^\dagger} \qquad\qquad 4.\,29.\,2$$

$$\mu = G_m = H^0 - \tfrac{5}{2}RT \ln \frac{T}{\Theta^\dagger} + RT \ln \frac{P}{P^\dagger} + BP \qquad 4.\,29.\,3$$

$$S_m = \tfrac{5}{2}R + \tfrac{5}{2}R \ln \frac{T}{\Theta^\dagger} - R \ln \frac{P}{P^\dagger} - P \frac{dB}{dT} \qquad 4.\,29.\,4$$

$$H_m = H^0 + \tfrac{5}{2}RT + \left(B - T \frac{dB}{dT}\right)P \qquad 4.\,29.\,5$$

$$C = \tfrac{5}{2}R - TP \frac{d^2B}{dT^2} \qquad\qquad 4.\,29.\,6$$

$$\lambda = e^{H^0/RT} \left(\frac{\Theta^-}{T}\right)^{\frac{5}{2}} \frac{p^\star}{P^\dagger} \qquad\qquad 4.\,29.\,7$$

Similarly by substitution of (2) into the formulae of § 4. 23 we derive

$$F_m = H^0 - RT - \tfrac{5}{2}RT \ln \frac{T}{\Theta^\dagger} + RT \ln \frac{RT}{P^\dagger V_m} + \frac{RTB}{V_m} \qquad 4.\,29.\,8$$

$$\mu = G_m = H^0 - \tfrac{5}{2}RT \ln \frac{T}{\Theta^\dagger} + RT \ln \frac{RT}{P^\dagger V_m} + \frac{2RTB}{V_m} \qquad 4.\,29.\,9$$

$$S_m = \tfrac{5}{2}R + \tfrac{5}{2}R \ln \frac{T}{\Theta^\dagger} - R \ln \frac{RT}{P^\dagger V_m} - R \frac{B}{V_m} - \frac{RT}{V_m} \frac{dB}{dT} \qquad 4.\,29.\,10$$

$$U_m = H^0 + \tfrac{3}{2}RT - \frac{RT^2}{V_m} \frac{dB}{dT} \qquad 4.\,29.\,11$$

$$C_V = \tfrac{3}{2}R - \frac{R}{V_m} \frac{d}{dT} \left(T^2 \frac{dB}{dT}\right) \qquad 4.\,29.\,12$$

We observe that S_m is independent of H^0.

§ 4. 30 DIATOMIC MOLECULES

For gases consisting of diatomic molecules $\lambda^\dagger$ has the form

$$\lambda^\dagger = e^{H^0/RT} \left(\frac{\Theta^\dagger}{T}\right)^{\frac{5}{2}} \lambda_r(T) \lambda_v(T) \qquad 4.\,30.\,1$$

where, as compared with (4. 29. 1), the extra factor $\lambda_r(T)$ is due to the two rotational degrees of freedom of the molecule and the extra factor $\lambda_v(T)$ is due to the vibrational degree of freedom of the molecule. We now describe these two factors in turn.

In connection with the rotational degree of freedom we define a characteristic temperature Θ_r by

$$\Theta_r = \frac{h^2}{8\pi^2 I k} = \frac{40.27 \text{ deg}}{10^{40} \, I/g \, cm^2} \qquad \text{4. 30. 2}$$

where I is the principle moment of inertia of the molecule, h is Planck's constant and k is Boltzmann's constant. Then, provided $T > 3\Theta_r$, with an accuracy of 1 % or better

$$\lambda_r(T) = \frac{\sigma \Theta_r}{T} \left(1 + \frac{1}{3} \frac{\Theta_r}{T} + \frac{1}{15} \frac{\Theta_r^2}{T^2} \right)^{-1} \quad (T \gg \Theta_r) \qquad \text{4. 30. 3}$$

where σ is a symmetry number equal to 2 for symmetrical molecules such as N_2 and 1 for unsymmetrical molecules such as CO.

Values of Θ_r for some typical diatomic molecules are given * in table 4. 2. From this we see that the condition for the validity of formula (3) is fulfilled for all gases, except hydrogen and deuterium, at all temperatures at which the gases can exist at conveniently measurable pressures. Even for hydrogen formula (3) is applicable with an accuracy of a few per cent at ordinary temperatures and better at higher temperatures. At lower temperatures, however, formula (3) may not be used for hydrogen. The thermodynamic properties of gaseous hydrogen and deuterium at low temperatures are complicated, not only owing to the failure of formula (3) but also owing to para-ortho separation. They will not be discussed here.

Turning now to the vibrational degree of freedom, we use another characteristic temperature Θ_v related to a characteristic vibrational frequency ν and wave number ν/c by

$$\Theta_v = \frac{h\nu}{k} = 1.4389 \frac{\nu}{c} \text{ deg cm} \qquad \text{4. 30. 4}$$

and $\lambda_v(T)$ is then given by

$$\lambda_v(T) = 1 - e^{-\Theta_v/T} \qquad \text{4. 30. 5}$$

* Values taken from Herzberg, *Molecular Spectra of Diatomic Molecules* 1950. Cf. Fowler and Guggenheim, *Statistical Thermodynamics* 1939 p. 90.
Cf. Slater, *Introduction to Chemical Physics* 1939 p. 136, observing that there Θ_{rot} is equal to twice our Θ_r.

In table 4. 2 values of Θ_v are given * for the various molecules. We see that at ordinary temperatures $T \ll \Theta_v$ and $\lambda_v(T)$ consequently does not differ much from unity except at high temperatures.

TABLE 4. 2

Characteristic temperatures Θ_r for rotation and Θ_v for vibration of typical diatomic molecules.

Formula	Θ_r/deg	$10^{-2}\,\Theta_v$/deg	σ
H_2	85.3	59.8	2
D_2	42.7	43.0	2
N_2	2.88	33.5	2
O_2	2 07	22.4	2
CO	2.77	30.8	1
NO	2 44	27.0	1
HCl	15.0	41.5	1
HBr	12.0	36.8	1
HI	9.29	32.1	1
Cl_2	0.344	7.96	2
Br_2	0 116	4.62	2
I_2	0.0537	3.07	2

By substituting (1), (3) and (5) into (4. 16. 10) we obtain

$$\mu^\dagger = RT \ln \lambda^\dagger = H^0 - RT \ln \frac{T^{\frac{7}{2}}}{\Theta^{\dagger\frac{5}{2}} \Theta_r \sigma}$$

$$- RT \ln \left(1 + \frac{1}{3}\frac{\Theta_r}{T} + \frac{1}{15}\frac{\Theta_r^2}{T^2}\right) + RT \ln\left(1 - e^{-\Theta v/T}\right) \qquad 4. 30. 6$$

If we expand the second logarithm, we obtain a constant term $-\frac{1}{3}R\Theta_r$ which may be absorbed into H^0. The next term in this expansion is $\frac{1}{90}\Theta_r^2/T^2$ and further terms are negligible. We thus obtain

$$\mu^\dagger = H^0 - RT \ln \frac{T^{\frac{7}{2}}}{\Theta^{\dagger\frac{5}{2}} \Theta_r \sigma} - \frac{1}{90}\frac{R\Theta_r^2}{T} + RT \ln\left(1 - e^{-\Theta v/T}\right) \quad 4. 30. 7$$

wherein the term $R\Theta_r^2/90T$ is in practice negligible. Omitting this term and substituting (7) into (4. 16. 2) we obtain

* Values taken from Herzberg, *Molecular Spectra of Diatomic Molecules* 1950.
Cf. Fowler and Guggenheim, *Statistical Thermodynamics* 1939 p. 90.
Cf. Slater, *Introduction to Chemical Physics* 1939 p. 142.

$$\mu = H^0 - RT \ln \frac{T^{\frac{7}{2}}}{\Theta^{\dagger\frac{5}{2}} \Theta_r \sigma} + RT \ln (1 - e^{-\Theta v/T})$$

$$+ RT \ln \frac{P}{P\dagger} + BP \qquad\qquad 4.\,30.\,8$$

From this we derive immediately

$$S_m = \tfrac{7}{2}R + R \ln \frac{T^{\frac{7}{2}}}{\Theta^{\dagger\frac{5}{2}} \Theta_r \sigma} - R \ln (1 - e^{-\Theta v/T}) + \frac{R\Theta_v/T}{e^{\Theta v/T} - 1}$$

$$R \ln \frac{P}{P\dagger} - P \frac{\mathrm{d}B}{\mathrm{d}T} \qquad\qquad 4.\,30.\,9$$

$$H_m = H^0 + \tfrac{7}{2}RT + \frac{R\Theta_v}{e^{\Theta v/T} - 1} + \left(B - T \frac{\mathrm{d}B}{\mathrm{d}T}\right) P \qquad 4.\,30.\,10$$

$$C = R \left\{ \frac{7}{2} + \frac{(\Theta_v/2T)^2}{\sinh^2 (\Theta_v/2T)} \right\} - T \frac{\mathrm{d}^2 B}{\mathrm{d}T^2} P \qquad 4.\,30.\,11$$

§ 4. 31 POLYATOMIC LINEAR MOLECULES

The formulae of the preceding section require only slight modification to apply to polyatomic linear molecules. We continue to write $\lambda\dagger$ in the form (4. 30. 1) and the rotational factor $\lambda_r (T)$ is precisely the same as for diatomic molecules. Typical values of Θ_r are given in table 4. 3, from which we see that normally $T \gg \Theta_r$. If the linear molecule contains a atoms, there will be $3a$—5 independent vibrational modes. Each such mode has a characteristic frequency ν with corresponding characteristic temperature Θ_v and each contributes a factor of the form (4. 30. 5) to $\lambda_v (T)$. Values of Θ_v are given [*] for typical molecules in table 4. 3.

We thus deduce

$$\mu\dagger = H^0 - RT \ln \frac{T^{\frac{7}{2}}}{\Theta^{\dagger\frac{5}{2}} \Theta_r \sigma} - \frac{1}{90} \frac{R\Theta_r^2}{T} + RT \sum_{\Theta_v} \ln (1 - e^{-\Theta v/T}) \qquad 4.\,31.\,1$$

wherein the summation extends over $3a$—5 characteristic temperatures Θ_v not necessarily all different. Omitting the negligible term in Θ_r^2 we obtain for the several thermodynamic functions

[*] Values taken from Herzberg, *Infra-red and Raman Spectra* 1945. Cf. Fowler and Guggenheim, *Statistical Thermodynamics* 1939 p. 112.

$$\mu = H^0 - RT \ln \frac{T^{\frac{7}{2}}}{\Theta^{\dagger\frac{5}{2}} \Theta_r \sigma} + RT \sum_{\Theta_v} \ln (1 - e^{-\Theta_v/T})$$

$$+ RT \ln \frac{P}{P\dagger} + BP \qquad \qquad 4.\ 31.\ 2$$

$$S_m = \tfrac{7}{2}R + R \ln \frac{T^{\frac{7}{2}}}{\Theta^{\dagger\frac{5}{2}} \Theta_r \sigma} - R \sum_{\Theta_v} \ln (1 - e^{-\Theta_v/T})$$

$$+ R \sum_{\Theta_v} \frac{\Theta_v/T}{e^{\Theta_v/T} - 1} - R \ln \frac{P}{P\dagger} - P \frac{dB}{dT} \qquad 4.\ 31.\ 3$$

$$H_m = H^0 + \tfrac{7}{2}RT + R \sum_{\Theta_v} \frac{\Theta_v}{e^{\Theta_v/T} - 1} + \left(B - T\frac{dB}{dT}\right)P \qquad 4.\ 31.\ 4$$

$$C = R\left\{\tfrac{7}{2} + \sum_{\Theta_v} \frac{(\Theta_v/2T)^2}{\sinh^2 (\Theta_v/2T)}\right\} - T\frac{d^2B}{dT^2} P \qquad 4.\ 31.\ 5$$

Each Σ denotes summation over $3a - 5$ terms for molecules composed of a atoms.

TABLE 4. 3

Characteristic temperatures Θ_r for rotation and Θ_v for vibration of typical polyatomic linear molecules.

Formula	Θ_r/deg	$10^{-2}\,\Theta_v$/deg	σ
		9.60	
		9.60	
OCO	0.560	20.0	2
		33.8	
		8.47	
		8.47	
NNO	0.602	18.5	1
		32.0	
		8.80	
		8.80	
		10.5	
HCCH	1.69	10.5	2
		28.4	
		47.3	
		48.5	

§ 4. 32 POLYATOMIC NON-LINEAR MOLECULES

A polyatomic non-linear molecule containing a atoms has 3 rotational degrees of freedom and $3a - 6$ vibrational degrees of freedom. We still write $\lambda^{\dagger}$ in the form (4. 30. 1), but the rotational factor $\lambda_r (T)$ is now given by

$$\lambda_r (T) = \frac{\sigma \Theta_r^{\frac{3}{2}}}{\pi^{\frac{1}{2}} T^{\frac{3}{2}}} \quad (T \gg \Theta_r) \qquad 4. 32. 1$$

We have omitted terms smaller by an order Θ_r/T, since the contribution of such terms can be absorbed into H^0, and have neglected terms smaller by an order Θ_r^2/T^2. In (1) the symmetry number σ is defined as the number of indistinguishable orientations of the molecule. For example σ is 1 for NOCl, 2 for OH_2, 3 for NH_3, 4 for C_2H_4, 6 for BF_3, 12 for CH_4, and 12 for C_6H_6. The characteristic temperature Θ_r is now defined by

$$\Theta_r = \frac{h^2}{8\pi^2 (I_1 I_2 I_3)^{\frac{1}{3}} k} = \frac{40.27 \text{ deg}}{10^{40} (I_1 I_2 I_3)^{\frac{1}{3}}/\text{g cm}^2} \qquad 4. 32. 2$$

where I_1, I_2, I_3 are the three principle moments of inertia of the molecule.

The vibrational factor $\Theta_v (T)$ is of the same form as for linear molecules except that there are $3a-6$ factors instead of $3a-5$.

We thus obtain for the several thermodynamic functions

$$\mu = H^0 - RT \ln \frac{\pi^{\frac{1}{2}} T^4}{\Theta^{\dagger \frac{5}{2}} \Theta_r^{\frac{3}{2}} \sigma} + RT \sum_{\Theta_v} \ln (1 - e^{-\Theta_v/T})$$

$$+ RT \ln \frac{P}{P^{\dagger}} + BP \qquad 4. 32. 3$$

$$S_m = 4R + R \ln \frac{\pi^{\frac{1}{2}} T^4}{\Theta^{\dagger \frac{5}{2}} \Theta_r^{\frac{3}{2}} \sigma} - R \sum_{\Theta_v} \ln (1 - e^{-\Theta_v/T})$$

$$+ R \sum_{\Theta_v} \frac{\Theta_v/T}{e^{\Theta_v/T} - 1} - R \ln \frac{P}{P^{\dagger}} - P \frac{dB}{dT} \qquad 4. 32. 4$$

$$H_m = H^0 + 4RT + R \sum_{\Theta_v} \frac{\Theta_v}{e^{\Theta_v/T} - 1} + \left(B - T \frac{dB}{dT} \right) P \qquad 4. 32. 5$$

$$C = R \left\{ 4 + \sum_{\Theta_v} \frac{(\Theta_v/2T)^2}{\sinh^2(\Theta_v/2T)} \right\} - T \frac{d^2B}{dT^2} P \qquad 4. 32. 6$$

Each Σ denotes summation over $3a$—6 terms for molecules composed of a atoms.

Values of Θ_r and Θ_v for some typical non-linear molecules are given [*] in table 4. 4. Even for OH_2, the molecule having the smallest moments of

TABLE 4. 4

Characteristic temperatures Θ_r for rotation and Θ_v for vibration of typical non-linear molecules

Formula	$\Theta_r/\deg$	$10^{-2}\,\Theta_v/\deg$	σ
NOCl		9 1	
		13.2	1
		26 2	
OH_2	22.3	22 9	
		52.5	2
		54.0	
NH_3	12 3	13 7	
		23 4	
		23 4	3
		48.0	
		49.1	
		49 1	

inertia, the condition $T \gg \Theta_r$ for formula (1) is satisfied at all practicable temperatures. The contributions of each vibrational mode to the several thermodynamic quantities may be read from table 4. 5, which gives the contributions to $-\mu/RT$, to H_m/RT, to S_m/R and to C/R all as functions of Θ_v/T.

§ 4. 33 ELECTRONIC CONTRIBUTIONS

We have hitherto tacitly ignored any possible contribution to the thermodynamic functions due to the electronic degrees of freedom. The contribution to μ, S_m and H_m is in fact zero for the vast majority of chemical substances not having a free valency; the electronic contributions may then be ignored. In particular this condition is fulfilled by the following molecules.

[*] Values taken from Herzberg, *Infra-red and Raman Spectra* 1945. Cf Fowler and Guggenheim, *Statistical Thermodynamics* 1939 pp. 113—114.

TABLE 4. 5

Contributions of a single harmonic oscillator to the several thermodynamic quantities expressed as functions of

$$x = \frac{h\nu}{kT} = \frac{\Theta_v}{T}$$

x	$-\mu/RT$ $= -\ln(1-e^{-x})$	H_m/RT $= \dfrac{x}{e^x - 1}$	S_m/R $= \dfrac{H_m - \mu}{RT}$	C/R $= \dfrac{(\frac{1}{2}x)^2}{\sinh^2(\frac{1}{2}x)}$
.01	4.610	0.995	5 605	1.000
.05	3.021	0.975	3.996	1 000
.1	2.352	0.951	3.303	0.999
.2	1.708	0 903	2.611	0 997
.3	1 350	0 857	2 208	0.993
.4	1.110	0.813	1.923	0.987
.5	0.933	0.771	1 704	0 979
.6	0 796	0.730	1 526	0.971
.7	0 686	0.691	1 377	0.960
.8	0.597	0.653	1.249	0.948
9	0.522	0.617	1.138	0 935
1.0	0.459	0.582	1 041	0 921
1.1	0.405	0.549	0 954	0 905
1.2	0.358	0.517	0 876	0.888
1 3	0.318	0 487	0 805	0.870
1.4	0.283	0 458	0.741	0 852
1.5	0 252	0.431	0.683	0 832
1.6	0.226	0 405	0 330	0 811
1.7	0.202	0.380	0.582	0 790
1.8	0.181	0 356	0.537	0 769
1.9	0 162	0.334	0.496	0 747
2.0	0.145	0.313	0 458	0.724
2.1	0.131	0.293	0.424	0 701
2.2	0 117	0.274	0 392	0.678
2 3	0.106	0.256	0.362	0.655
2 4	0.095	0.239	0 335	0.632
2.5	0.086	0 224	0.309	0 609
2.6	0 077	0.209	0 286	0.586
2.7	0.070	0 195	0.264	0.563
2.8	0.063	0.181	0.244	0 540
2 9	0.057	0.169	0.225	0 518
3.0	0.051	0.157	0.208	0.496
3 2	0.042	0.136	0 178	0.454
3.4	0.034	0 117	0 151	0.413
3.6	0.028	0 101	0.129	0.374
3.8	0.023	0.087	0.110	0 338
4.0	0.018	0 075	0 093	0 304
4.5	0.011	0 051	0.062	0.230
5.0	0.007	0.034	0 041	0.171
5.5	0.004	0.023	0 027	0.125
6.0	0.002	0 015	0.017	0.090
6.5	0.002	0.010	0.013	0.064
7.0	0 001	0.006	0.007	0 045

(a)   The monatomic molecules He, Ne, A, Kr, Xe, Zn, Cd, Hg.

(b)   The diatomic molecules H_2, D_2, Li_2, Na_2, K_2, N_2, F_2, Cl_2, Br_2, I_2, CO, HCl, HBr, HI.

(c)   The polyatomic inorganic molecules OH_2, SH_2, NH_3, PH_3, CH_4, CO_2, N_2O, CS_2, SO_2.

(d)   All organic molecules, including those containing double or triple bonds, other than those classed as free radicals.

The one notably exceptional molecule, which according to its chemical behaviour is regarded as having no free valencies, is O_2. Whereas the normal states of all the molecules mentioned above are singlets, the normal state of O_2 is $^3\Sigma$. As a result of this, λ contains an extra factor $\frac{1}{3}$, while μ contains an extra term $- RT \ln 3$ and S_m contains an extra term $R \ln 3$. As long as we are considering only gaseous oxygen these extra factors and terms, being constant, are physically irrelevant. It is only when we come to consider the equilibrium between gaseous oxygen and solid oxygen or chemical equilibria between oxygen and other gases that these extra contributions become physically significant.

There are also electronic contributions in the case of molecules having a single free valency. This has the form of an extra factor $\frac{1}{2}$ in λ, an extra term $- RT \ln 2$ in μ and an extra term $R \ln 2$ in S_m in the case of all the following molecules.

(a)   The univalent atoms Li, Na, K, Tl.

(b)   Organic free radicals such as CH_3 and $C(C_6H_5)_3$.

On the other hand in the case of the free halogen atoms the electronic contributions are not so simple *. The contribution to λ is an extra factor

$$(4 + 2e^{-\Theta_e/T})^{-1} \qquad\qquad 4.\,33.\,1$$

where Θ_e is an electronic characteristic temperature. The values of Θ_e are as follows:

$$\begin{aligned}
\text{Cl} \quad & \Theta_e = 1.28 \times 10^3 \text{ deg} \\
\text{Br} \quad & \Theta_e = 5.2 \ \times 10^3 \text{ deg} \\
\text{I} \quad & \Theta_e = 10.9 \ \times 10^3 \text{ deg}
\end{aligned}$$

We see that for temperatures up to 1000 °K, it is only in the case of Cl that the second term in (1) is not negligible. For Br and I the factor in λ reduces effectively to $\frac{1}{4}$. The corresponding terms in μ and S_m are $- RT \ln 4$ and $R \ln 4$ respectively.

* See Fowler and Guggenheim, *Statistical Thermodynamics* 1939 p 201.

We have still to mention the odd molecule NO. The extra factor in λ is

$$\tfrac{1}{2} (1 + e^{-\Theta_e/T})^{-1} \qquad\qquad 4.\,33.\,2$$

with $\Theta_e = 178$ deg. Thus at very low temperatures this factor is effectively $\tfrac{1}{2}$ and at very high temperatures it is effectively $\tfrac{1}{4}$. As the temperature is raised there are especially rapid increases in S_m and in H_m in the neighbourhood of 178 °K.

In conclusion we may mention that even in the case of the most stable saturated molecules, there is in principle an electronic factor in λ of the form

$$(1 + ge^{-\Theta_e/T})^{-1} \qquad\qquad 4.\,33.\,3$$

where g is a small integer, but the characteristic temperature Θ_e is so large that this factor differs insignificantly from unity.

§ 4. 34 PRESSURE DEPENDENCE FOR CONDENSED PHASES

We turn now from gases to condensed phases and shall later consider the equilibrium between a condensed phase and a gas. As we shall see in § 4. 48, there are conditions of temperature and pressure called critical at which all distinction between gas and liquid disappears, but except at conditions close to the critical there is a rather sharp contrast between the properties of a gas and a liquid. The contrast between gas and crystal is always a sharp one.

Whereas the isothermal compressibility $\varkappa$ of a gas is at least roughly equal to the reciprocal of the pressure, the isothermal compressibility of a solid and that of a liquid, except near the critical temperature, are much smaller than that of a gas and is less dependent on the pressure. For a condensed phase, whether solid or liquid, we may therefore usually assume

$$-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \varkappa = \text{constant} \qquad\qquad 4.\,34.\,1$$

We can integrate (1) at constant temperature to obtain

$$V = V^\dagger e^{-\varkappa P} \qquad (T \text{ const.}) \qquad 4.\,34.\,2$$

where $V^\dagger$ is the limiting value of V at vanishing pressure and of course depends on the temperature. Since moreover at all ordinary pressures $\varkappa P \ll 1$, we may, without loss of accuracy, replace (2) by the more convenient relation

$$V = V^\dagger \, (1 - \varkappa P) \qquad\qquad 4.\,34.\,3$$

or for one mole

$$V_m = V_m^\dagger \, (1 - \varkappa P) \qquad\qquad 4.\,34.\,4$$

We can integrate again with respect to P at constant T and obtain using (1. 36. 12)

$$\mu = \mu^\dagger + PV_m^\dagger \, (1 - \tfrac{1}{2}\varkappa P) = \mu^\dagger + P\,[V_m] \qquad 4.\,34.\,5$$

where $\mu^\dagger$ is the limiting value of μ at vanishing pressure and depends only on the temperature, while $[V_m]$ denotes the value of V_m at a pressure equal to $\tfrac{1}{2}P$.

For typical liquids $\varkappa$ is about 10^{-4} atm^{-1} and for many solids is even smaller. Hence even at pressures of several atmospheres, the terms in $\varkappa P$ may usually be neglected.

Multiplying (4) by P and subtracting from (5) we obtain

$$F_m = \mu^\dagger + \tfrac{1}{2}\varkappa P^2 V_m^\dagger \qquad\qquad 4.\,34.\,6$$

where again the term containing $\varkappa$ is almost always negligible.

According to the definition of the coefficient of thermal expansion a,

$$\frac{\mathrm{d}V^\dagger}{\mathrm{d}T} = a^\dagger V^\dagger \qquad\qquad 4.\,34.$$

where $a^\dagger$ is the value of a for vanishing pressure. At ordinary temperatures not near the critical a is nearly independent of temperature and is about 10^{-3} deg^{-1}. For many purposes the variation of volume with temperature is negligible.

At temperatures well below the critical, V_m in a typical liquid or solid is between 10 and 100 cm^3 mole^{-1}, so that at atmospheric pressure PV_m is usually less than 0.1 atm l. whereas at ordinary temperatures RT is about 20 atm l. Thus for a condensed phase at atmospheric pressure PV_m is usually less than and often much less than 1% of RT. For this reason PV_m is for many purposes negligible and it is then unnecessary to distinguish between the values of μ and F_m or between the values of H_m and U_m.

If we differentiate (5) with respect to T, we obtain

$$S_m = -\frac{\mathrm{d}\mu^\dagger}{\mathrm{d}T} - aP\,[V_m] = -\frac{\mathrm{d}\mu^\dagger}{\mathrm{d}T} - aPV_m^\dagger \, (1 - \tfrac{1}{2}\varkappa P) \qquad 4.\,34.\,8$$

where a must strictly be given its value at a pressure equal to $\tfrac{1}{2}P$, but usually the variation of a with pressure may be ignored. At

ordinary pressures and even at quite high pressures the last term in (8) will be negligible and we may write

$$S_m = -\frac{d\mu^\dagger}{dT} - aPV_m^\dagger \qquad\qquad 4.\,34.\,9$$

From (9) and (5) we obtain

$$H_m = \mu^\dagger - T\frac{d\mu^\dagger}{dT} + PV_m^\dagger\,(1 - \tfrac{1}{2}\varkappa P - aT) \qquad 4.\,34.\,10$$

where the terms containing P and especially those containing $\varkappa$ and a will usually be negligible.

§ 4. 35 TEMPERATURE DEPENDENCE FOR LIQUIDS

We have seen that the dependence of the thermodynamic properties of condensed phases on the pressure is simple and usually unimportant. We have now to consider how these properties depend on the temperature.

As regards liquids there is nothing fundamental or general that can be said except that μ can often be represented over quite a wide range of temperature by an empirical relation of the form

$$\mu = A - (B{-}C)T - CT \ln T + PV_m \qquad (A, B, C \text{ const.}) \qquad 4.\,35.\,1$$

where we have neglected the compressibility. From (1) we deduce neglecting thermal expansion

$$S_m = B + C \ln T \qquad\qquad (B, C \text{ const.}) \qquad 4.\,35.\,2$$

$$H_m = A + CT + PV_m \qquad\qquad (A, C \text{ const.}) \qquad 4.\,35.\,3$$

According to this empirical approximation the molar heat capacity C is independent of the temperature. We have already mentioned in § 4. 05 that for many liquids, in particular water, C is nearly independent of the temperature.

The approximate constancy of C and the consequent validity of relations of the form (1), (2), (3) also hold for many solids at ordinary and higher temperatures, but not at low temperatures. This accident has in the past caused undue importance to be attached to the heat capacity, in contrast to the heat function H and the entropy S. The only real importance of C is that it is the connecting link between H and S, as explained in § 4. 05. This link is especially simple when C is independent of T, but this occurrence, however frequent, is of no fundamental importance.

§ 4. 36 CRYSTALS AT VERY LOW TEMPERATURES

It is predicted by statistical theory and borne out by experiment that at very low temperatures the heat function of a crystalline solid varies linearly with the fourth power of the absolute temperature. That is to say, neglecting the small dependence on pressure,

$$H_m = H_m^0 + \tfrac{1}{4}aT^4 \qquad \text{(small } T\text{)} \qquad 4.\,36.\,1$$

where a is a constant and H_m^0 is the limiting value of H_m as $T \to 0$. Correspondingly we have for the entropy

$$S_m = S_m^0 + \tfrac{1}{3}aT^3 \qquad \text{(small } T\text{)} \qquad 4.\,36.\,2$$

where S_m^0 is the limiting value of S_m as $T \to 0$. The formulae (1) and (2) are not independent, but are related through the thermodynamic formula (4. 04. 2)

$$T\mathrm{d}S = \mathrm{d}H \qquad \text{(const. } P\text{)} \qquad 4.\,36.\,3$$

From (1) and (2) it immediately follows that

$$\mu = H_m^0 - TS_m^0 - \tfrac{1}{12}aT^4 \qquad \text{(small } T\text{)} \qquad 4.\,36.\,4$$

We have not stated how small T must be for these formulae to hold, nor is it possible to make any precise statement since the requirement is different for different substances. For most substances investigated these formulae appear to be at least approximately valid at temperatures below 20 °K.

We shall see later that a comparison between the constant S_m^0 in (2) and the constant $\mathrm{d}\mu^\dagger/\mathrm{d}T$ occurring in the formula for the molar entropy of a gas is of considerable interest. For this reason it is important to be able to extrapolate experimental data on the entropy from the lowest experimental temperature down to 0 °K. For this purpose one determines a suitable value of the constant a from the relation (1) by plotting H against T^4 in the lowest temperature range in which experimental measurements have been made. This value of a is then used in (2) to give experimental values of $S(T)—S(0)$. Provided the experimental data extend below 20 °K, the contribution to S from this extrapolation is usually so small that an accurate estimate of a is not required.

Actually the most important feature of the formulae of this section is not their precise form, still less the value of a, but the fact that S tends rapidly towards a constant value as T decreases. This behaviour

is in striking contrast with the formulae for the entropy of gases at ordinary temperatures which contain terms in $\ln T$.

§ 4. 37 CRYSTALS AT INTERMEDIATE TEMPERATURES. DEBYE'S MODEL

In the previous section we have described the thermodynamic behaviour of crystals at very low temperatures. In § 4. 35 we mentioned briefly that at ordinary and higher temperatures the behaviour of many solids, as well as liquids, is represented at least approximately by the formulae of that section corresponding to a temperature-independent heat capacity. In the intermediate range the heat capacity increases with temperature, but its rate of increase falls rather rapidly. There is no precise quantitative theory except for the simplest crystals consisting of monatomic molecules. Even for these the accurate theory is so complicated as to be of little practical use and it is in fact usually replaced by a much simpler approximation due to Debye.

We shall not here describe Debye's model, still less discuss * its limitations, but shall give the formulae which follow from it. The formulae contain apart from the temperature T, two parameters namely the energy U_m^0 of the crystal at $T = 0$ and a characteristic temperature Θ_D. Both these parameters U_m^0 and Θ_D are functions of the molar volume V_m, but are independent of the temperature. In considering Debye's model it is therefore expedient to regard as independent variables T, V instead of the usually more practically convenient T, P. We accordingly begin by writing down Debye's formula for the molar free energy F_m of a crystal

$$F_m \quad U_m^0 - TS_m^0 + 3RT \int_0^{\Theta_D} \ln(1 - e^{-\theta/T}) \frac{3\theta^2}{\Theta_D^3} \, d\theta \qquad 4. 37. 1$$

wherein we repeat that U_m^0 and Θ_D are functions of V_m whereas S_m^0 on the other hand is a constant independent of V_m, as well as of T, and depends only on the arbitrary zero of entropy.

From (1) we could derive the pressure by the relation

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = -\left(\frac{\partial F_m}{\partial V_m}\right)_T \qquad 4. 37. 2$$

We have however seen in § 4. 34 that the thermodynamic properties of a condensed phase, in particular a crystal, are nearly independent of

* See Blackman, *Rep. Progr. Phys.* 1942 **8** 11.

the pressure; more precisely $PV_m \ll RT$. We may consequently regard the pressure as negligible and replace (2) by the condition

$$\left(\frac{\partial F_m}{\partial V_m}\right)_T = 0 \qquad 4.\,37.\,3$$

which gives an equilibrium relation between U^0 and Θ_D. From (1) and (3) we find that this relation is

$$\frac{\partial U_m^0}{\partial V_m} = 3R \, \frac{\partial \Theta_D}{\partial V_m} \int_0^{\Theta_D} \frac{1}{e^{\theta/T} - 1} \, \frac{3\theta^3 \, d\theta}{\Theta_D^4} \qquad 4.\,37.\,4$$

From (1) we can derive formulae for the other thermodynamic functions, in particular

$$U_m - U_m^0 = 3R \int_0^{\Theta_D} \frac{1}{e^{\theta/T} - 1} \, \frac{3\theta^3 \, d\theta}{\Theta_D^3} \qquad 4.\,37.\,5$$

$$S_m - S_m^0 = -3R \int_0^{\Theta_D} \left\{ \ln\left(1 - e^{-\theta/T}\right) - \frac{\theta/T}{e^{\theta/T} - 1} \right\} \frac{3\theta^2 \, d\theta}{\Theta_D^3} \qquad 4.\,37.\,6$$

$$C_V = 3R \int_0^{\Theta_D} \frac{(\theta/2T)^2}{\sinh^2(\theta/2T)} \, \frac{3\theta^2 \, d\theta}{\Theta_D^3} \qquad 4.\,37.\,7$$

We may note that at very low temperatures, $T \ll \Theta_D$ and we may without sensible error replace the upper limits of integration in the above formulae by ∞. We thus obtain

$$U_m = U_m^0 + 3R \, \frac{T^4}{\Theta_D^3} \int_0^\infty \frac{3\xi^3 \, d\xi}{e^\xi - 1} = U_m^0 + 3R \, \frac{T^4}{\Theta_D^3} \, \frac{\pi^4}{5} \qquad 4.\,37.\,8$$

which, in view of the negligible difference between U_m and H_m is in agreement with (4. 36. 1) with a given by

$$\tfrac{1}{4}a = \frac{3\pi^4 R}{5\Theta_D^3} \qquad 4.\,37.\,9$$

While we shall not here discuss the extent of agreement or disagreement to be expected between these formulae and the behaviour of real crystals, we shall however devote some space to the consideration of how the comparison can most directly be made. Let us therefore consider which quantities are most directly measurable, bearing in mind that with all condensed phases it is convenient to make measurements at constant pressure but extremely difficult to make measurements at constant volume.

The usual calorimetric measurements determine directly how H depends on T. Provided these measurements have been carried to a low enough temperature, the extrapolation to $T = 0$ can be performed as described in § 4. 36 so that we know $H_m(T) - H_m^0$ as a function of T. Then by using the relation (4. 36. 3) we can *without any further experimental data* compute $S_m(T) - S_m^0$. We can now compare this experimental quantity with the right side of (4. 37. 6), which is tabulated as a function of Θ_D/T. We thus obtain for each temperature T a value of Θ_D which fits the experimental value of $S_m - S_m^0$. These values of Θ_D will be constant neither in practice, nor according to Debye's model. For we are considering data at constant pressure, consequently at varying volume, and, as the volume varies, so Θ_D varies. In fact as the volume increases, theory predicts that Θ_D should steadily decrease. If then it is found that as T increases, the value of Θ_D, determined as described above, slowly but steadily decreases then we may say that at least there is no contradiction between the experimental data and the model. If on the other hand as T increases, the value of Θ_D thus determined increases or fluctuates, then we may say with certainty that the experimental data are in disagreement with the model.

We give typical illustrations of this method of comparison in tables 4. 6 and 4. 7 for gold * and magnesium † respectively. We observe that for gold Θ_D rises from 163° to 173° and then falls again to 167°. For magnesium Θ_D decreases steadily from 360° to 318°. In a few cases, such as copper and lead, Θ_D varies even less than in the case of gold. In other cases, notably lithium, Θ_D varies by nearly 20 %.

We would emphasize that the entropy is the only simple thermodynamic function for which we have both a closed formula and an experimental value obtainable from a single set of calorimetric measurements performed at constant pressure. In spite of the directness and simplicity of the above method of comparison, it is not generally used. The usual procedure is, from the experimental measurements of H as a function of T, first to compute $dH/dT = C_P$; then by measured, or estimated values of a and $\varkappa$ to use formula (4. 09. 3) to compute C_V from C_P; lastly to compare the C_V so calculated with formula (7). There are two objections to this procedure as compared with that recommended here. In the first place the computation of C_P from H involves a differentiation and so increases any experimental errors

* Clusius and Harteck, *Z. phys. Chem.* 1928 **134** 243.

† Clusius and Vaughen, *J. Amer. Chem. Soc.* 1930 **52** 4686.

TABLE 4. 6

Comparison of molar entropy of gold with Debye's formula

$\frac{T}{°K}$	$\frac{(S_m - S_m^0)/R}{\text{expt.}}$	$\frac{\Theta_D}{T}$	$\frac{\Theta_D}{\text{deg}}$
15	0.06	10 90	163
20	0 14	8.25	165
30	0 385	5 57	167
40	0 705	4 225	167
50	1 05	3 39	170
60	1.40	2 87	172
70	1.73	2 45	171
80	2.03	2 15	172
90	2.32	1.91	172
100	2.58	1 72	172
120	3 07	1.44	173
140	3 49	1 23	172
160	3 87	1.075	172
180	4 22	0 95	171
200	4 53	0 855	171
300	5.77	0.555	167

TABLE 4 7

Comparison of molar entropy of magnesium with Debye's formula

$\frac{T}{°K}$	$\frac{(S_m - S_m^0)/R}{\text{expt}}$	$\frac{\Theta_D}{T}$	$\frac{\Theta_D}{\text{deg}}$
20	0 01	18.0	360
30	0 05	11.5	345
40	0 13	8.38	335
50	0 26	6.53	326
60	0 41	5.41	324
80	0 77	4 03	322
100	1 15	3 22	322
120	1 52	2.68	322
140	1 87	2.30	322
160	2 20	2.00	320
180	2 50	1.78	320
200	2.76	1.61	322
300	7.77	1.06	318

whereas in the computation of S from H the integration helps to smooth out the errors introduced by the differentiation. In the second place the computation of C_V from C_P by means of (4. 09. 3) requires either several other pieces of experimental data or else some guess work, neither of which is required if one makes comparisons of entropy. When the value of C_V, thus computed or estimated, is compared with formula (7) we can calculate at each temperature a value of Θ_D which fits. Just as in the comparison of entropies, these values of Θ_D should, if the model is good, decrease slowly and steadily as the temperature, and so the volume, increases. There appears to be a widespread, but mistaken belief that Θ_D should be independent of temperature in spite of the thermal expansion.

Quite apart from the change in Θ_D due to thermal expansion, variations of Θ_D with temperature are to be expected owing to the limitations of Debye's model. In view of all the complications in the lattice theory Debye's theory is remarkable not in the extent of its failure, but rather in the extent of its success *.

§ 4. 38 CORRESPONDING TEMPERATURES OF CRYSTALS

We have seen that Debye's model is only an approximate representation of a simple crystal of monatomic molecules and further that even if it were an accurate representation, the characteristic temperature Θ_D should still vary with temperature owing to thermal expansion. Nevertheless it is an experimental fact that Debye's formulae with constant Θ_D do give a remarkably good approximate representation over a wide temperature range of the actual behaviour of many simple crystals, especially metals crystallizing in the cubic system. For such substances the values of $S - S^0$, of $(H - H^0)/T$ and consequently of $(\mu - \mu^0)/T$ or of $Y - Y^0$ are universal functions of T/Θ_D. Thus several important thermodynamic properties of different crystals have the same value when T/Θ_D has the same value. Temperatures of different substances such that T/Θ_D has the same value are called *corresponding temperatures*. The principle that certain thermodynamic properties have equal values for different substances at corresponding temperatures is called a *principle of corresponding temperatures*. It is to be observed that this principle for simple crystals makes no reference to the pressure, which is tacitly assumed to be low and to have no appreciable effect on the values of the properties under discussion. In

* See Blackman, *Rep. Progr. Phys.* 1942 8 11.

§ 4. 53 we shall discuss a more interesting principle of corresponding temperatures and corresponding pressures for liquids and gases.

§ 4. 39 COMPARISON OF DEBYE'S FUNCTIONS WITH EINSTEIN'S

Debye's model was preceded by a simpler model due to Einstein leading to the simpler formulae

$$F_m = U_m^0 - TS_m^0 + 3RT \ln (1 - e^{-\Theta_E/T}) \qquad 4.\,39.\,1$$

$$U_m - U_m^0 = 3R\Theta_E/(e^{\Theta_E/T} - 1). \qquad 4.\,39.\,2$$

$$S_m - S_m^0 = -3R \{\ln (1 - e^{-\Theta_E/T}) - \Theta_E/T (e^{\Theta_E/T} - 1)\} \qquad 4.\,39.\,3$$

$$C_V = 3R \frac{(\Theta_E/2T)^2}{\sinh^2 (\Theta_E/2T)} \qquad 4.\,39.\,4$$

where Θ_E is Einstein's characteristic temperature.

By comparing Debye's formulae with Einstein's we observe that the former contain integrals from zero to Θ_D where the latter contain merely simple functions of Θ_E. Thus Θ_E in a sense represents an average Θ covering the range from 0 to Θ_D. Thus at any given temperature the value of Θ_E which fits is always smaller than the value of Θ_D which fits.

If one tries to fit the experimental data by Einstein's formulae with a constant Θ_E one fails completely at the lowest temperatures, but at higher temperatures there is little to choose between Einstein's formulae and Debye's, provided the value chosen for Θ_E is suitably adjusted. In fact when $T > \frac{1}{3}\Theta_D$ the values of $U_m - U_m^0$ calculated from Debye's formula do not differ appreciably from the values calculated from Einstein's formula provided one uses for Θ_E the value given by $\Theta_E = 0.73\Theta_D$. Similarly when $T > \frac{1}{3}\Theta_D$ the values of $S_m - S_m^0$ calculated from Debye's formula do not differ appreciably from the values calculated from Einstein's formula provided one takes $\Theta_E = 0.71\Theta_D$. The comparison is shown in table 4. 8. The slight difference of about 2 % between the best values of Θ_E corresponding to a given Θ_D in the cases of the energy and the entropy is a measure of the accuracy lost by the substitution. If one takes $\Theta_E = 0.72\Theta_D$, the difference between the values calculated by the two formulae for the free energy are even less than for the energy and the entropy. Since in any case the experimental data cannot be fitted exactly by a constant value of Θ_D, considerable simplification can often be attained without significant loss of accuracy by using Einstein's

TABLE 4. 8

Comparison of Einstein's formulae with Debye's assuming
$\Theta_E = 0.73\ \Theta_D$ for energies
and $\Theta_E = 0.71\ \Theta_D$ for entropies

$\dfrac{\Theta_D}{T}$	$\dfrac{U_m - U_m^0}{3RT}$		$\dfrac{S_m - S_m^0}{3R}$	
	Debye	Einstein	Debye	Einstein
0.1	.964	963	3.64	3.64
0.2	.929	.929	2.945	2.95
0.4	.860	.861	2.26	2.26
0.6	.794	.797	1 85	1.86
0.8	.733	.736	1.575	1.58
1.0	675	.679	1 36	1.37
1.2	.620	.625	1.19	1.19
1.4	.571	575	1.045	1.045
1.6	525	.527	0 925	0.925
1.8	.482	483	0.825	0.820
2 0	.442	.442	0.735	0.730
2.2	.405	.403	0 657	0.650
2.4	.371	.368	0.590	0.580
2.6	.339	.334	0.529	0.518
2.8	.310	.304	0.476	0.463
3.0	.284	.276	0.429	0.414

formulae rather than Debye's provided one is concerned only with temperatures greater than $\frac{1}{3}\Theta_D$. At lower temperatures Debye's formulae should be used in preference to Einstein's.

§ 4. 40 EQUILIBRIUM BETWEEN TWO PHASES

Having discussed the thermodynamic properties of a single phase, we now turn to consider two phases in equilibrium. If we denote the two phases by superscripts α and β, the condition for equilibrium between the two phases is according to (1. 45. 5)

$$\mu^\alpha = \mu^\beta \qquad \qquad 4.\ 40.\ 1$$

or according to (4. 15. 7)

$$\lambda^\alpha = \lambda^\beta \qquad \qquad 4.\ 40.\ 2$$

Since in any single phase of a pure substance the temperature T and pressure P may be varied independently and μ or λ may be regarded as a function of T, P, we may therefore regard (1) or (2) as expressing a relation between T and P for equilibrium between the two phases.

It follows that when the two phases are in equilibrium, the temperature T and pressure P are not independently variable but either determines the other. We accordingly say that a single phase of one component has two *degrees of freedom* but a pair of phases of one component has only one *degree of freedom*.

§ 4. 41 RELATION BETWEEN TEMPERATURE AND PRESSURE FOR TWO PHASE EQUILIBRIUM

We now proceed to determine how the equilibrium pressure between two phases a and β depends on the temperature T. Differentiating (4. 40. 1) we have

$$d\mu^a = d\mu^\beta \qquad \text{4. 41. 1}$$

or

$$\frac{\partial\mu^a}{\partial T}\,dT + \frac{\partial\mu^a}{\partial P}\,dP = \frac{\partial\mu^\beta}{\partial T}\,dT + \frac{d\mu^\beta}{\partial P}\,dP \qquad \text{4. 41. 2}$$

Using (1. 36. 11) and (1. 36. 12), we obtain

$$- S_m^a\,dT + V_m^a\,dP = - S_m^\beta\,dT + V_m^\beta\,dP \qquad \text{4. 41. 3}$$

or

$$(V_m^\beta - V_m^a)\,dP = (S_m^\beta - S_m^a)\,dT \qquad \text{4. 41. 4}$$

Formula (4) can also be obtained more directly from Maxwell's relation (3. 04. 3)

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \qquad \text{4. 41. 5}$$

We apply this relation to a system consisting of the two phases a and β in equilibrium with each other. Since for this equilibrium to persist P is completely determined by T and is independent of V, we may replace the partial differential coefficient $(\partial P/\partial T)_V$ by dP/dT. Moreover at constant temperature, and incidentally also constant pressure, S and V can only change through some quantity of substance passing from the phase a to the phase β or conversely. Thus the ratio of the changes in S and in V is independent of the quantity transferred from the one phase to the other. If then we denote by the symbol Δ the increase of any property when unit quantity passes from the phase a to the phase β, we have

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{\Delta S}{\Delta V} \qquad \text{4. 41. 6}$$

and so (5) becomes

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} \qquad 4.\,41.\,7$$

which is formula (4) in different notation.

Since we may rewrite (4. 40. 1) as

$$H_m^a - TS_m^a = H_m^\beta - TS_m^\beta \qquad 4.\,41.\,8$$

it follows immediately that

$$T\Delta S = T\,(S_m^\beta - S_m^a) = H_m^\beta - H_m^a = \Delta H \qquad 4.\,41.\,9$$

This relation has an obvious physical meaning, the same as that of (4. 04. 3). If unit quantity passes isothermally from the phase a to the phase β, the heat q absorbed is equal to ΔH because the process occurs at constant pressure and it is also equal to $T\Delta S$ because, the system being in equilibrium throughout, the change is reversible.

If we now substitute from (9) into (7), we obtain

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} = \frac{H_m^\beta - H_m^a}{T\,(V_m^\beta - V_m^a)} \qquad 4.\,41.\,10$$

which is known as *Clapeyron's relation*. This can also be obtained more directly by starting from

$$\frac{\mu^a}{T} = \frac{\mu^\beta}{T} \qquad 4.\,41.\,11$$

instead of (4. 40. 1). Differentiating (11) we obtain

$$\frac{\partial\,(\mu^a/T)}{\partial T}\,dT + \frac{1}{T}\frac{\partial\mu^a}{\partial P}\,dP = \frac{\partial\,(\mu^\beta/T)}{\partial T}\,dT + \frac{1}{T}\frac{\partial\mu^\beta}{\partial P}\,dP \qquad 4.\,41.\,12$$

and so using (1. 36. 15) and (1. 36. 12)

$$-\frac{H_m^a}{T^2}\,dT + \frac{V_m^a}{T}\,dP = -\frac{H_m^\beta}{T^2}\,dT + \frac{V_m^\beta}{T}\,dP \qquad 4.\,41.\,13$$

whence (10) follows immediately. We have given these alternative derivations of (10) because of its great importance, as the prototype of other similar formulae in systems of more than one component.

§ 4. 42 CLAPEYRON'S RELATION APPLIED TO TWO CONDENSED PHASES

Let us consider the application of Clapeyron's relation to the equi-librium between a solid and a liquid. Using the supercripts ^{S} and ^{L}

to denote these two phases, we have for the variation of the equilibrium pressure with the equilibrium temperature according to (4. 41. 10)

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{H_m^L - H_m^S}{T(V_m^L - V_m^S)} = \frac{\Delta_f H}{T(V_m^L - V_m^S)} = \frac{\Delta_f S}{V_m^L - V_m^S} \qquad 4.\,42.\,1$$

where $\Delta_f H$ is the *molar heat of fusion* and $\Delta_f S$ is the *molar entropy of fusion*. Since fusion is always an endothermic process, the numerator of (1) is always positive, but the denominator may have either sign. It is negative for water, but positive for most substances. Thus the melting point of ice is decreased by increase of pressure, but that of most solids is increased.

The application of Clapeyron's relation to the equilibrium between two solid phases is analogous. In (1) we need only make the superscript L denote the phase stable at the higher temperature and S the phase stable at the lower temperature, so that $H_m^L - H_m^S$ is positive. The sign of $\mathrm{d}P/\mathrm{d}T$ will then be the same as that of $V_m^L - V_m^S$.

For condensed phases, both V_m^L and V_m^S are small and their difference is much smaller. Usually a pressure of some hundred atmospheres is required to change the freezing point by a single degree. As an illustrative example, let us consider water. We have

$$-\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{22\ \mathrm{J\ deg^{-1}\ mole^{-1}}}{(19.6 - 18.0)\ \mathrm{cm^3\ mole^{-1}}} = \frac{22\ \mathrm{J}}{1.6\ \mathrm{cm^3\ deg}}$$

$$= \frac{220\ \mathrm{atm}}{1.6\ \mathrm{deg}} = 1.4 \times 10^2\ \frac{\mathrm{atm}}{\mathrm{deg}} \qquad 4.\,42.\,2$$

As a second example, let us take sodium. We have

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{7.1\ \mathrm{J\ deg^{-1}\ mole^{-1}}}{(24.6 - 24.2)\ \mathrm{cm^3\ mole^{-1}}} = \frac{7.1}{0.4}\ \frac{\mathrm{J}}{\mathrm{cm^3\ deg}}$$

$$= \frac{71\ \mathrm{atm}}{0.4\ \mathrm{deg}} = 1.8 \times 10^2\ \frac{\mathrm{atm}}{\mathrm{deg}} \qquad 4.\,42.\,3$$

Hence as long as the pressure does not exceed one or two atmospheres, the freezing point may for many purposes be regarded as unaffected by the pressure.

§ 4. 43 CLAPEYRON'S RELATION APPLIED TO VAPOUR EQUILIBRIUM

Let us now consider the equilibrium between a liquid and a gaseous phase. Using the superscripts ^{L} for the liquid and ^{G} for the gas we have according to (4. 41. 10)

$$\frac{dP}{dT} = \frac{H_m^G - H_m^L}{T(V_m^G - V_m^L)} \qquad 4.43.1$$

This exact relation can be transformed by making two approximations. In the first place we neglect the molar volume of the liquid compared with that of the vapour. In the second place we neglect the virial coefficients of the gas and treat it as perfect. With these approximations we have

$$V_m^G - V_m^L \simeq V_m^G \simeq RT/P \qquad 4.43.2$$

Substituting (2) into (1), we obtain

$$\frac{1}{P}\frac{dP}{dT} = \frac{H_m^G - H_m^L}{RT^2} = \frac{\Delta_e H}{RT^2} \qquad 4.43.3$$

where $\Delta_e H$ is the *molar heat of evaporation*.

It will prove convenient to have a symbol other than P to denote equilibrium vapour pressure of a condensed phase and for this purpose we shall use p. We accordingly write in place of (3)

$$\frac{d \ln p}{dT} = \frac{\Delta_e H}{RT^2} \qquad 4.43.4$$

or

$$\frac{d \ln p}{d(1/T)} = -\frac{\Delta_e H}{R} \qquad 4.43.5$$

It follows from (5) that if we plot $\ln p$ against $1/T$ the curve so obtained has at each point a slope equal to $-\Delta_e H/R$. Actually $\Delta_e H$ varies so slowly with the temperature that this curve is nearly a straight line.

Formula (5) incidentally provides a method, rarely if ever mentioned, for determining the molar mass in the vapour. For by measuring p at several known temperatures we can use (5) to calculate $\Delta_e H$. We can then make direct calorimetric measurements to determine what mass of liquid is converted to vapour when a quantity of heat equal to $\Delta_e H$ is absorbed. This mass is then one mole of vapour.

The treatment of equilibrium between a solid and its vapour is

precisely analogous. The vapour pressure p of the solid is related to the temperature by

$$\frac{\mathrm{d}\ln p}{\mathrm{d}\,(1/T)} = -\frac{\Delta_s H}{R} \qquad 4.\,43.\,6$$

where $\Delta_s H$ is the *molar heat of sublimation*.

§ 4. 44 HEAT CAPACITIES OF TWO PHASES IN EQUILIBRIUM

Consider two phases of a single component in mutual equilibrium. Suppose now that we isolate a portion of either of these phases and change its temperature, not at constant pressure, but adjusting the pressure to the value corresponding to two phase equilibrium at each temperature. The quantity of heat absorbed in this phase will evidently be proportional to the number of moles in the phase and, for a small temperature increase $\mathrm{d}T$, proportional to $\mathrm{d}T$. We may therefore write for either of the two phases

$$q = nC_{eq}\,\mathrm{d}T \qquad 4.\,44.\,1$$

where n is the number of moles in the phase and C_{eq} is the *molar heat capacity at two phase equilibrium*. Since moreover the change is reversible we may write instead of (1)

$$T\mathrm{d}S = nC_{eq}\,\mathrm{d}T \qquad 4.\,44.\,2$$

or

$$\mathrm{d}S_m = C_{eq}\,\mathrm{d}T/T \qquad 4.\,44.\,3$$

But for the change in question

$$\mathrm{d}S_m = \left\{ \left(\frac{\partial S_m}{\partial T}\right)_P + \left(\frac{\partial S_m}{\partial P}\right)_T \frac{\mathrm{d}P}{\mathrm{d}T} \right\}\mathrm{d}T \qquad 4.\,44.\,4$$

Comparing (3) with (4) we see that

$$C_{eq} = T\left\{ \left(\frac{\partial S_m}{\partial T}\right)_P + \left(\frac{\partial S_m}{\partial P}\right)_T \frac{\mathrm{d}P}{\mathrm{d}T} \right\} = C_P - aV_m T \frac{\mathrm{d}P}{\mathrm{d}T} \qquad 4.\,44.\,5$$

using the definition (4. 05. 2) of C_P and Maxwell's relation (3. 04. 4). Now substituting from (4. 41. 10) into (5) we obtain

$$C_{eq} = C_P - aV_m \frac{\Delta H}{\Delta V} \qquad 4.\,44.\,6$$

where Δ denotes the increase when one mole passes isothermally from

the one phase to the other; as regards sign the same convention must of course be used for ΔH and ΔV.

§ 4. 45 HEAT CAPACITIES AT SATURATION

The most important application of the formulae of the previous section is to the equilibrium between a liquid and its vapour. The quantities C_{eq} are then called the *molar heat capacities at saturation* and are denoted by C_{sat}. If we neglect the second virial coefficient of the gas and also neglect the molar volume of the liquid compared with that of the gas, formula (4. 44. 6) becomes

$$C_{sat} = C_P - a \frac{PV_m}{RT} \Delta_e H \qquad \text{4. 45.}$$

where $\Delta_e H$ is the molar heat of evaporation.

Formula (1) is applicable either to the vapour or to the liquid, but the importance of the second term on the right is very different in the two cases. For the vapour we have, still neglecting the second virial coefficient,

$$a = T^{-1} \qquad PV_m = RT \qquad \text{4. 45. 2}$$

so that, using the superscript ^{G} for the gas, we obtain

$$C_{sat}^G = C_P^G - \frac{\Delta_e H}{T} = C_P^G - \Delta_e S \qquad \text{4. 45. 3}$$

The second term on the right may be numerically greater than the first, in which case C_{sat}^G is negative. For example for steam at its normal boiling point.

$$C_P = 34 \text{ J deg}^{-1} \text{ mole}^{-1}$$

$$\Delta_e S = \frac{\Delta_e H}{T} = \frac{40.6 \text{ kJ mole}^{-1}}{373 \text{ deg}} = 109 \text{ J deg}^{-1} \text{ mole}^{-1}$$

so that

$$C_{sat}^G = (34 - 109) \text{ J deg}^{-1} \text{ mole}^{-1} = -75 \text{ J deg}^{-1} \text{ mole}^{-1}$$

and we see that the heat capacity of steam at saturation is negative.

For the liquid phase on the other hand the second term on the right of (1) is incomparably smaller than for the gas because V_m is smaller by a factor of something like 10^{-3} or less. Consequently for the liquid phase we may neglect this term and replace (1) by

$$C_{sat}^L = C_P^L \qquad \text{4. 45. 4}$$

where the superscript ^{L} denotes the liquid phase.

The formulae of this section may also be applied to the equilibrium conditions between solid and vapour. Formula (3) is then applicable to the vapour and formula (4) to the solid.

§ 4. 46 TEMPERATURE DEPENDENCE OF HEATS OF EVAPORATION AND OF FUSION

Consider any phase change such as evaporation or fusion and let the symbol Δ denote the increase in any property when one mole passes isothermally from the one phase to the other in the direction such that ΔH is positive, i.e. from liquid to gas or from solid to liquid. Then we have

$$\Delta H / T = \Delta S \qquad \qquad 4.\,46.\,1$$

Differentiating with respect to T, varying P so as to maintain equilibrium, we have

$$\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{\Delta H}{T}\right) = \frac{\mathrm{d}}{\mathrm{d}T}\,\Delta S = \Delta\,\frac{\mathrm{d}S}{\mathrm{d}T} = \frac{\Delta C_{\mathrm{eq}}}{T} \qquad 4.\,46.\,2$$

or

$$\frac{\mathrm{d}}{\mathrm{d}T}\,\Delta H - \frac{\Delta H}{T} = \Delta C_{\mathrm{eq}} \qquad \qquad 4.\,46.\,3$$

For equilibrium between liquid and vapour, $C_{\mathrm{eq}} = C_{\mathrm{sat}}$ is given by (4. 45. 3) for the vapour and by (4. 45. 4) for the liquid. Substituting these into (3) we obtain

$$\frac{\mathrm{d}}{\mathrm{d}T}\,\Delta_{\mathrm{e}}H = C_P^{\mathrm{G}} - C_P^{\mathrm{L}} \qquad \qquad 4.\,46.\,4$$

the terms $\Delta_{\mathrm{e}}H/T$ on either side cancelling. Formula (4) involves the several approximations mentioned in § 4. 45. It is formally similar to the exact formula for a process taking place between pressure limits independent of the temperature.

To obtain the temperature coefficient of a heat of fusion, we have to go back to (4. 44. 6), which we rewrite in the form

$$C_P = C_P - \left(\frac{\partial V_m}{\partial T}\right)_P \frac{\Delta_{\mathrm{f}}H}{\Delta_{\mathrm{f}}V} \qquad \qquad 4.\,46.\,5$$

where Δ_{f} denotes the increase of a molar quantity on fusion. Substituting (5) into (3), we obtain

$$\frac{\mathrm{d}}{\mathrm{d}T}\,\Delta_{\mathrm{f}}H = \Delta_{\mathrm{f}}C_P + \frac{\Delta_{\mathrm{f}}H}{T} - \Delta_{\mathrm{f}}H\left(\frac{\partial \ln \Delta_{\mathrm{f}}V}{\partial T}\right)_P \qquad 4.\,46.\,6$$

a formula due to Planck *. The last term on the right will usually be very small compared with the second and may then be neglected. We then obtain the approximation

$$\frac{d}{dT} \Delta_t H = \Delta_t C_P + \frac{\Delta_t H}{T}$$

4. 46. 7

Of the two terms on the right, either may be numerically greater. We thus have a formula not even approximately of the same form as the formula for a process taking place between pressure limits independent of the temperature.

Evidently the formulae of this section may mutatis mutandis be applied to the equilibrium between two solid phases.

§ 4. 47 TRIPLE POINT

We have seen that the equilibrium condition for a single component between two phases α and β

$$\mu^\alpha (T, P) = \mu^\beta (T, P)$$

4. 47. 1

is equivalent to a relation between P and T which can be represented by a curve on a $P - T$ diagram. Similarly the equilibrium between the phases α and γ can be represented by a curve on a $P - T$ diagram. If these two curves cut, we shall have at the point of intersection

$$\mu^\alpha (T, P) = \mu^\beta (T, P) = \mu^\gamma (T, P)$$

4. 47. 2

and the three phases α, β, γ will be in mutual equilibrium. This point of intersection is called a *triple point* and the values of T and P at the triple point are called the *triple-point temperature* and the *triple-point pressure*.

We have seen that a single component in one phase has two degrees of freedom since temperature and pressure can be varied independently and that two phases in mutual equilibrium have only one degree of freedom since temperature and pressure are mutually dependent. We now see that three phases can exist in mutual equilibrium only at a particular temperature and particular pressure. Thus three phases of a single component in mutual equilibrium have no degrees of freedom.

In fig. 4. 4 the conditions of mutual equilibrium for H_2O are shown † on the $P - T$ diagram.

Triple points can also exist for two solid phases and one liquid phase or for two solid phases and a vapour phase or for three solid phases.

* Planck, *Ann. Phys., Lpz* 1887 **30** 574
† From Landolt-Börnstein *Tables*.

More rarely we may have two liquid phases and a vapour phase or a solid phase. A triple point can occur in a region where all three phases
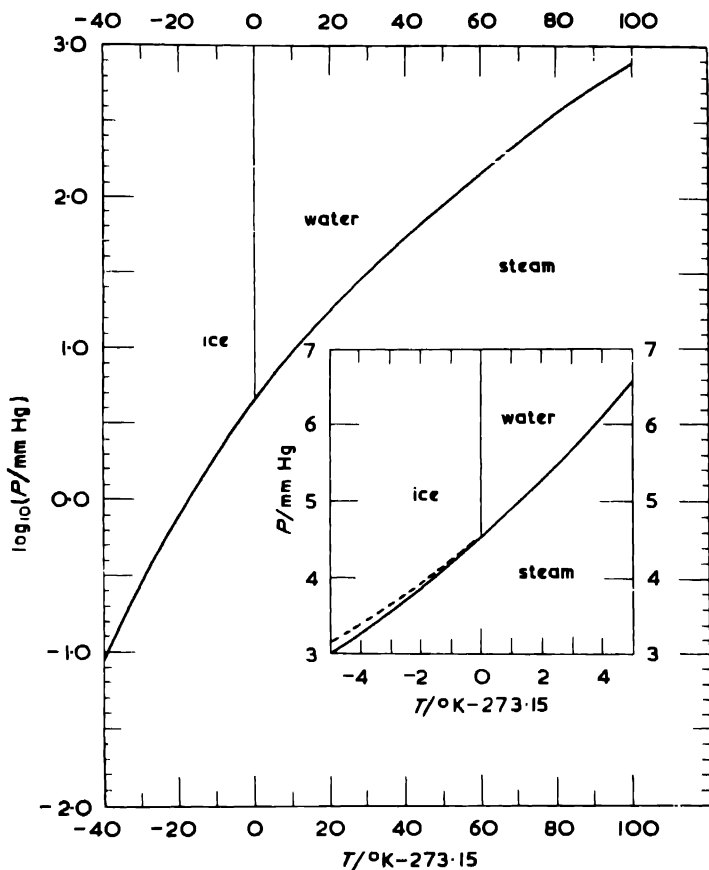
Fig 4. 4   Equilibrium between ice, water and steam.

are metastable. The conditions of equilibrium for sulphur * are shown in fig 4. 5. There are three stable triple points

T_1: equilibrium between monoclinic, liquid and vapour

T_2: equilibrium between rhombic, monoclinic and liquid

T_3: equilibrium between rhombic, monoclinic and vapour

and one metastable triple point

T_4: equilibrium between rhombic, liquid and vapour all three phases being metastable and the monoclinic being the stable form.

* From Landolt-Bornstein *Tables*.

§ 4. 48 CRITICAL POINT

The $P - V_m$ isotherms of all pure substances fall into two classes according as the temperature lies above or below a *critical temperature*
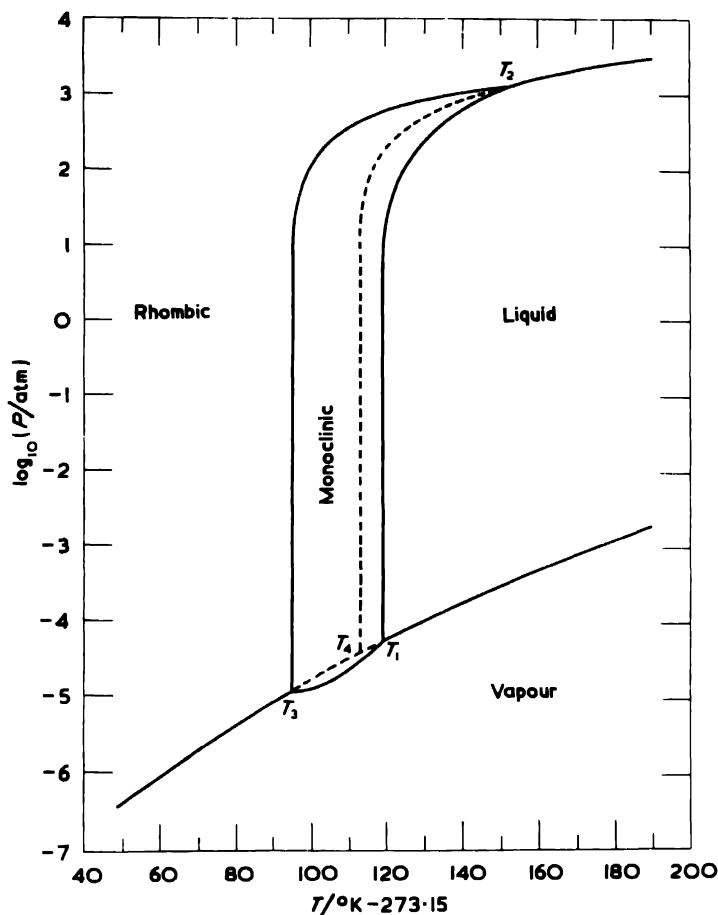
Fig. 4. 5   Phase equilibria of sulphur.

T_c. Examples of each class for carbon dioxide * are shown in fig. 4. 6.

When the molar volume is sufficiently large both classes approximate to the rectangular hyperbolae $PV_m = RT$ of a perfect gas. As the molar volume diminishes, the form of the two classes is quite different. At temperatures greater than the critical, there is a smooth regular vari-

* Michels, Blaisse and Michels, *Proc Roy. Soc.* A 1937 **160** 367.

ation along the whole isotherm, which can be expressed mathematically by saying that it is a single analytic curve or expressed physically by saying that throughout the isotherm there is a single gaseous phase.
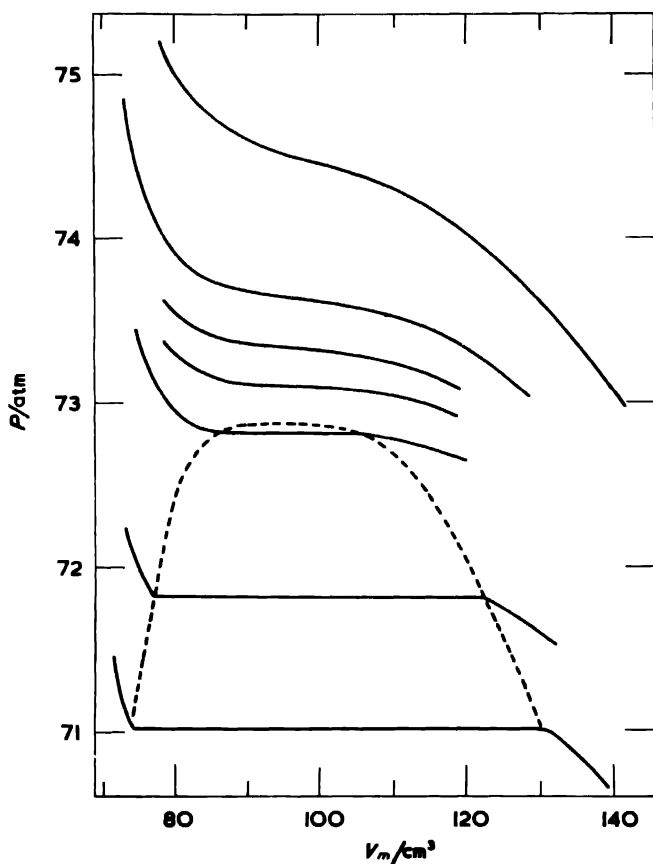
Fig. 4. 6. Isotherms of carbon dioxide.

At temperatures below the critical on the other hand, the isotherm consists of three analytically distinct parts separated by discontinuities of the slope. The middle portion is a straight line parallel to the V_m axis. These parts represent respectively the pure gas, the saturated vapour in equilibrium with the liquid and the pure liquid. The isothermal curve for the *critical temperature* T_c is the borderline between the two classes of isotherms. In this isotherm the horizontal portion is reduced to a single point of horizontal inflexion.

The broken curve is on the left the locus of the points representing the liquid phase under the pressure of its vapour and on the right the locus of the points representing the saturated vapour. As the temperature increases the molar volume of the liquid at the pressure of its vapour increases, while the molar volume of the saturated vapour decreases. At the critical temperature the isotherm has a point of horizontal inflexion at the top of the broken curve where the liquid and vapour phases cease to be distinguishable. The state represented by this point is called the *critical state*; the pressure and molar volume in the critical state are called the *critical pressure* P_c and the *critical volume* V_c respectively.

To recapitulate, above the critical temperature the substance can exist in only one state, the gaseous. Below the critical temperature it can exist in two states, the liquid with a molar volume less than the critical volume and the gas with a molar volume greater than the critical volume. The equilibrium pressure between the two phases, liquid and vapour can have values up to but not exceeding the critical pressure.

§ 4. 49 CONTINUITY OF STATE

The relation between pressure P and molar volume V_m of a single component at a temperature below the critical temperature is shown diagrammatically in fig. 4. 7. The portion KL represents the liquid state, the portion VW the gaseous state, and the straight portion LV the two phase system liquid + saturated vapour.

At the given temperature the substance can only be brought from the liquid state to the gaseous state, or, conversely, by a change during part of which two separate phases will be present. By varying the temperature, however, it is possible to bring the substance from the gaseous state represented by W to the liquid state represented by K by a continuous change throughout which there is never more than one phase present. It is only necessary to raise the temperature above the critical temperature, keeping the volume sufficiently greater than the critical volume, then compress the fluid to a volume below the critical volume, keeping the temperature above the critical temperature and finally cool the liquid to its original temperature, keeping the volume sufficiently below the critical volume. This possibility of continuity between the liquid and gaseous states was first realized by James Thomson, and he suggested that the portions KL and VW of the isotherm are actually parts of one smooth curve, such as KLMONVW.

In point of fact, states corresponding to the portion VN are realizable as *supersaturated vapour*, and under certain circumstances the same may be true of the portion LM representing *superheated liquid*. Each
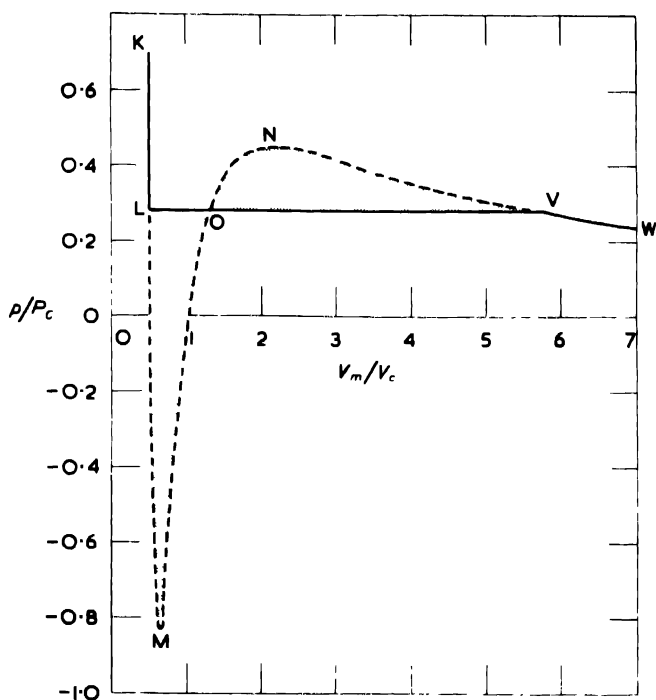
Fig 4 7 Continuity between liquid and gas phases.

of these portions represents states stable with respect to infinitesimal variations, but metastable relative to the two phase system liquid + saturated vapour. The portion of the curve MON, on the other hand, represents states absolutely unstable, since here

$$\frac{\partial V_m}{\partial P} > 0 \qquad\qquad 4.\,49.\,1$$

and, according to (4. 02. 4), such states are never realizable.

Although the states represented by points on the curve LMONV are either metastable or unstable, still they are equilibrium states. It follows that the sequence of states represented by the curve LMONV corresponds to a reversible process. The change in the chemical potential μ of the fluid in passing through this sequence of states is, according to (1. 36. 12), given by

$$\mu^G - \mu^L = \int \left(\frac{\partial \mu}{\partial P}\right)_T dP = \int V_m \, dP \qquad \text{4. 49. 2}$$

where the integrals are to be evaluated along the curve LMONV. But, since the two states represented by ^{L} and ^{G} can exist in equilibrium with each other, we have

$$\mu^G = \mu^L \qquad \text{4. 49. 3}$$

From (2) and (3) we deduce

$$\int V_m \, dP = 0 \qquad \text{4. 49. 4}$$

where the integral is to be evaluated along the curve LMONV. The geometrical significance of (4) is that the two shaded surfaces LMO and ONV are of equal area. This condition is due to Maxwell *.

It is instructive to consider *continuity of state* in terms of the free energy F. Imagine F to be plotted as vertical coordinate against T and V as horizontal Cartesian coordinates. The resulting locus is a curved surface. Consider now cross-sections of this surface by planes $T = \text{const.}$ Examples of these are shown diagrammatically in fig. 4. 8 and since

$$\left(\frac{\partial F}{\partial V}\right)_T = -P \qquad \text{4. 49. 5}$$

the slope of each curve at each point is equal to $-P$.

In the upper curve we see that as V increases, the negative slope steadily decreases numerically and so P decreases steadily. This is typical of any temperature above the critical.

In the lower curve we see that there are two portions K'L' and V'W' in which the negative slope decreases steadily as V increases and these are joined by a straight line L'V' touching K'L' at L' and touching V'W' at V' .These three portions correspond to liquid, to gas and to a two phase liquid-vapour system. This is typical of a temperature below the critical. The broken portion of curve L'M' represents super-heated liquid and the broken portion V'N' represents supersaturated vapour. We see immediately that all states represented by these portions of curve are metastable, for any point on either of them lies above a point of the same volume V on the straight line L'V'. This means that the free energy of the superheated liquid or supersaturated

* Maxwell, *Nature* 1875 **11** 357.

vapour is greater than a system of the same volume consisting of a mixture of liquid L' and saturated vapour V'.
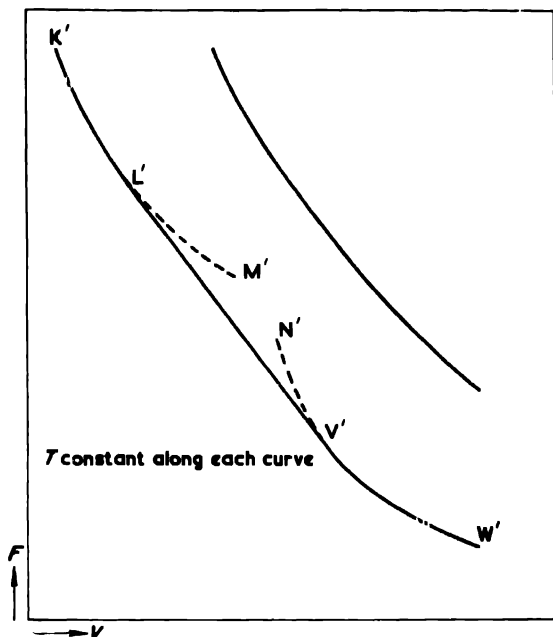
Fig. 4. 8. Stable and metastable isotherms.

The portions of curve L'M' and N'V' have curvature concave upwards so that

$$\frac{\partial P}{\partial V} = -\frac{\partial^2 F}{\partial V^2} < 0 \qquad\qquad 4.\ 49.\ 6$$

Hence according to (4. 02. 4) they represent states internally stable, though metastable with respect to a two phase mixture. If however we wish to unite these two portions into a single smooth curve, the middle portion would necessarily have a curvature concave downwards. This would correspond to a positive value of $\partial P/\partial V$ and so to unstable states and we saw in § 1. 43 that such states are never realizable. It may therefore be argued that no physical significance could be attached to this part of the $F - T - V$ surface. Nevertheless, if the realizable parts K'L'M' and N'V'W' of the surface could be represented by the *same analytical function*, it would be reasonable from a mathematical point of view to consider the complete surface. Having constructed such a surface and considering a section corresponding to a particular temperature below the critical, we could then plot $P = -\partial F/\partial V$ against

V and so construct a curve such as that in fig. 4. 7. From this construction it follows of necessity that in fig. 4. 7 the area below the broken curve LMONV and the area below the straight line LV are both equal to the height of L′ above V′ in fig. 4. 8. Consequently these two areas are equal. From this it follows immediately that the two shaded areas are equal as already proved. Since the portion MON of the curve cannot be realized experimentally, instead of saying that the two phase equilibrium is determined by the condition of equality of the two shaded areas, it is perhaps more correct to say that, L and V being known, if the connecting portion of the curve were sketched in such a manner as to make the two shaded areas unequal it would be nonsensical, for then —P would not be the slope of any conceivable curve on the $F — V$ diagram.

§ 4. 50 TWO PHASES AT DIFFERENT PRESSURES

In our previous considerations of equilibrium between two phases of one component, we have assumed the equilibrium to be complete so that the two phases were at the same pressure. The distribution equilibrium of one component between two phases at different pressures is also of interest. Let us denote the two phases by the superscripts ^{a} and $^\beta$. Then the equilibrium condition determining the change from the one phase to the other is according to (1. 46. 1)

$$\mu^a = \mu^\beta \qquad \qquad 4.\ 50.\ 1$$

If we vary the common temperature T of the two phases and the pressures P^a and P^β of the two phases, the condition for maintenance of equilibrium is

$$d\mu^a = d\mu^\beta \qquad \qquad 4.\ 50.\ 2$$

or

$$\frac{\partial \mu^a}{\partial T}\, dT + \frac{\partial \mu^a}{\partial P^a}\, dP^a = \frac{\partial \mu^\beta}{\partial T}\, dT + \frac{\partial \mu^\beta}{\partial P^\beta}\, dP^\beta \qquad \qquad 4.\ 50.\ 3$$

Substituting from (1. 36. 11) and (1. 36. 12) we obtain

$$- S_m^a\, dT + V_m^a\, dP^a = - S_m^\beta\, dT + V_m^\beta\, dP^\beta \qquad \qquad 4.\ 50.\ 4$$

or

$$V_m^\beta\, dP^\beta - V_m^a\, dP^a = (S_m^\beta - S_m^a)\, dT = \underset{a \to \beta}{\Delta S}\, dT \qquad \qquad 4.\ 50.\ 5$$

where $\underset{a \to \beta}{\Delta}$ is used to denote the increase of a quantity when one mole passes from the phase a to the phase β.

Since we may rewrite (1) as

$$H_m^a - TS_m^a = H_m^\beta - TS_m^\beta \qquad \text{4. 50. 6}$$

it follows immediately that

$$T\Delta S = T\left(S_m^\beta - S_m^a\right) = H_m^\beta - H_m^a = \Delta H \qquad \text{4. 50. 7}$$
$$\underset{a \to \beta}{} \qquad\qquad\qquad\qquad \underset{a \to \beta}{}$$

just as for two phases at the same pressure. In fact formula (4. 41. 9) is a special example of (7) and the physical significance is the same in both cases.

If we now substitute from (7) into (5) we obtain

$$V_m^\beta \, dP^\beta - V_m^a \, dP^a = \Delta H \, dT/T \qquad \text{4. 50. 8}$$
$$\underset{a \to \beta}{}$$

It is evident that two of the three quantities T, P^a, P^β are independent and so the system has two degrees of freedom. The most important application of these formulae is to the equilibrium between a liquid and its vapour. We then use the superscript ^{L} for the liquid and ^{G} for the vapour. We also use P to denote the pressure on the liquid and p the pressure of the vapour. In this notation (8) becomes

$$V_m^G \, dp - V_m^L \, dP = \frac{\Delta_e H}{T} \, dT \qquad \text{4. 50. 9}$$

where $\Delta_e H$ is the molar heat of evaporation. According to the definition of fugacity $p^\star$ and (4. 22. 5), we may replace (9) by

$$RTd \ln p^\star - V_m^L \, dP = \frac{\Delta_e H}{T} \, dT \qquad \text{4. 50. 10}$$

In particular at constant temperature we have for the dependence of the fugacity of the gas on the external pressure P on the liquid

$$\left(\frac{\partial \ln p^\star}{\partial P}\right)_T = \frac{V_m^L}{RT} \qquad \text{4. 50. 11}$$

If we treat the vapour as a perfect gas, we may replace $p^\star$ by p.

If, on the other hand, we maintain constant the pressure P on the liquid, we obtain from (10) for the dependence of the gas fugacity on the temperature

$$\frac{d \ln p^\star}{dT} = \frac{\Delta_e H}{RT^2} \qquad \text{(const. } P\text{)} \qquad \text{4. 50. 12}$$

or if we treat the vapour as a perfect gas

$$\frac{\mathrm{d} \ln p}{\mathrm{d} T} = \frac{\Delta_\mathrm{e} H}{RT^2} \qquad \text{(const. } P\text{)} \qquad \text{4. 50. 13}$$

or

$$\frac{\mathrm{d} \ln p}{\mathrm{d} (1/T)} = - \frac{\Delta_\mathrm{e} H}{R} \qquad \text{(const. } P\text{)} \qquad \text{4. 50. 14}$$

It is instructive to compare (14) with (4. 43. 5). The latter involves neglecting the molar volumes of the liquid compared with that of the vapour, but the former involves no such approximation. The difference between the exact formula (14) and the approximate formula (4. 43. 5) is negligible owing to the fact that in order to affect the saturated vapour pressure p appreciably by change of the hydrostatic pressure P at constant temperature, one requires according to (11) pressures considerably greater than the vapour pressure itself.

The direct experimental application of these formulae would require the separation of the liquid from the vapour by a membrane permeable to the vapour, but not to the liquid. This is difficult to achieve, though not impossible. Consequently the formulae have not much direct practical application. They have nevertheless a real importance, which will become clear when we consider systems of two or more components. We shall find that these formulae remain true in the presence of another component gas insoluble in the liquid, provided we interpret p as the *partial pressure* of the vapour when mixed with the inert gas. We cannot profitably say more at this stage, but we shall return to this point in § 5. 22.

§ 4. 51 FUGACITY OF A CONDENSED PHASE

In § 4. 22 we defined the fugacity of a gaseous pure substance in terms of its absolute activity λ. We now define the fugacity of a pure substance in any condensed phase as being equal to the fugacity in the gas phase with which it is in equilibrium. Evidently when two condensed phases are in equilibrium with each other the fugacities must be equal in the two phases.

With this extended definition we may regard formula (4. 50. 10), namely

$$\mathrm{d} \ln p^* = \frac{\Delta_\mathrm{e} H}{RT^2}\, \mathrm{d} T + \frac{V_m^\mathrm{L}}{RT}\, \mathrm{d} P \qquad \text{4. 51. 1}$$

as expressing the dependence of the fugacity p^* of a liquid on the

temperature T and the external pressure P. A precisely analogous equation applies to a solid.

§ 4. 52 VAN DER WAALS' AND DIETERICI'S EQUATIONS OF STATE

Many attempts have been made in the past to represent the equation of state of gas and liquid throughout the whole $P - V - T$ domain by an analytical formula. It is now known that it is not possible so to represent the experimental data accurately except by complicated and unwieldy formulae of little interest. On the other hand the distinction between liquid and gas and the existence of a critical point can be deduced *qualitatively* from various quite simple equations of state. Of these we shall mention the two simplest, namely the equation of van der Waals, already referred to in § 4. 20,

$$P + \frac{a}{V_m^2}\Big)(V_m - b) = RT \qquad\qquad 4.\,52.\,1$$

and the equation of Dieterici

$$P\,(V_m - b) = RT \exp\left(- a/RTV_m\right) \qquad\qquad 4.\,52.\,2$$

At low pressures, both these equations reduce to

$$V_m = \frac{RT}{P} + b - \frac{a}{RT} \qquad\qquad 4.\,52.\,3$$

when we neglect second order small terms. We have already discussed formula (3) in § 4. 20. It is equivalent to writing for the second virial coefficient B

$$B = b - \frac{a}{RT} \qquad\qquad 4.\,52.\,4$$

We mentioned in § 4. 18 that the temperature dependence of B can not be represented by a formula such as (4). Nor has either of the equations (1) and (2) any sound theoretical basis except at low pressures and high temperatures. It is also well known that neither van der Waals' nor Dieterici's equation can be made to fit the experimental data over any wide domain of T, P. It might however be hoped that by regarding a, b as slowly varying functions of T, P it would be possible to represent the experimental data over a small region by suitably chosen values of a and b. There is in fact a widespread belief that a and b can be so chosen as to represent the actual behaviour at the critical point. We shall now show that this belief has some measure

of justification in the case of Dieterici's equation, but none whatever in the case of van der Waals' equation.

We have seen in § 4. 48 that at the critical point the isotherm on the $P - V$ diagram is a point of horizontal inflexion. We therefore have the critical conditions

$$\frac{\partial P}{\partial V}\bigg)_T = 0 \qquad\qquad 4.\,52.\,5$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 \qquad\qquad 4.\,52.\,6$$

If we substitute (1) into (5) and (6) we obtain

$$\frac{RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} = 0 \qquad\qquad 4.\,52.\,7$$

$$\frac{2RT_c}{(V_c - b)^3} - \frac{6a}{V_c^4} = 0 \qquad\qquad 4.\,52.\,8$$

From these we obtain immediately

$$b = \tfrac{1}{3}V_c \qquad a = \tfrac{9}{8}RT_c V_c \qquad\qquad 4.\,52.\,9$$

Substituting (9) into (1) we obtain van der Waals' equation in the alternative form

$$\left(P + \frac{9}{8}\frac{RT_c V_c}{V_m^2}\right)(V_m - \tfrac{1}{3}V_c) = RT \qquad\qquad 4.\,52.\,10$$

In particular by setting $V_m = V_c$ and $T = T_c$ we obtain for P_c

$$P_c = \frac{3}{8}\frac{RT_c}{V_c} \qquad\qquad 4.\,52.\,11$$

or

$$\frac{P_c V_c}{RT_c} = \frac{3}{8} \qquad\qquad 4.\,52.\,12$$

Adopting a similar procedure with Dieterici's equation, we substitute (2) into (5) and (6). After some simple algebraic reduction we obtain

$$\frac{a}{RT_c} = \frac{V_c^2}{V_c - b} = \frac{V_c^2}{2\,(V_c - b)^3} \qquad\qquad 4.\,52.\,13$$

whence

$$b = \tfrac{1}{2}V_c \qquad a = 2RT_c V_c \qquad\qquad 4.\,52.\,14$$

Substituting (14) into (2), we obtain Dieterici's equation in the alternative form

$$P (V_m - \tfrac{1}{2}V_c) = RT \exp (-2T_c V_c/TV_m) \qquad 4.\,52.\,15$$

In particular by setting $V_m = V_c$ and $T = T_c$ we obtain for P_c

$$P_c = \frac{2RT_c}{V_c} e^{-2} \qquad 4.\,52.\,16$$

or

$$\frac{P_c V_c}{RT_c} = 2\,e^{-2} \qquad 4.\,52.\,17$$

Thus according to van der Waals' equation the value of the ratio $P_c V_c/RT_c$ is 0.375 and according to Dieterici's equation it is 0.271. We shall see in § 4. 53 that for the gases with the simplest molecules the experimental value of this ratio is nearly 0.29. For the majority of non-polar substances the experimental values lie between 0.25 and 0.30. We see then that in this respect Dieterici's equation gives at least a rough representation of the observed relation between P_c, V_c and T_c whereas van der Waals' equation does not.

Unfortunately one still meets sometimes the statement that van der Waals' constants a and b were computed from the critical data. Such a statement is at least ambiguous, if not nonsensical; for since van der Waals' equation gives a false value of $P_c V_c/RT_c$ one can evidently obtain various inconsistent sets of values for a, b according as these are computed from P_c, V_c or from P_c, T_c or from V_c, T_c.

§ 4. 53 CORRESPONDING STATES

The *principle of corresponding states* asserts that for a group of similar substances the equation of state can be written in the form

$$\frac{P}{P_c} = \varphi \left(\frac{T}{T_c}, \frac{V_m}{V_c} \right), \qquad 4.\,53.\,1$$

where φ is the same function for all the substances of the group.

Since according to (4. 52. 10) and (4. 52. 12) van der Waals' equation of state can be written in the form

$$\frac{P}{P_c} + 3\,\frac{V_c^2}{V_m^2}\right) \left(\frac{V_m}{V_c} - \frac{1}{3} \right) = \frac{8}{3}\frac{T}{T_c} \qquad 4.\,53.\,2$$

it follows that a group of substances all conforming to this equation would obey the principle of corresponding states. Since however no

such substances exist, this is of no physical interest. The like may be said of Dieterici's equation which can be written in the form

$$\frac{P}{P_c}\left(\frac{V_m}{V_c} - \frac{1}{2}\right) = \frac{1}{2} \exp\left(2 - 2T_c V_c / T V_m\right) \qquad 4. 53. 3$$

or in fact of any other proposed equation of state containing just two adjustable parameters.

Although, as we have already mentioned, it is not possible to express the equation of state in any simple analytical form, the principle of corresponding states is obeyed with a useful degree of accuracy by a considerable number of substances. It is in fact obeyed within the accuracy of experiment by the three inert elements A, Kr, Xe and to a high degree of accuracy by these substances together with Ne, N_2, O_2, CO and CH_4. It would be misleading to try to divide substances sharply into two groups, those which do and those which do not obey the principle. It is obeyed more or less accurately by a great variety of substances. Deviations occur due to any one or several of the following causes

(a) quantal effects in the lightest molecules, especially H_2, He and to a much smaller extent Ne

(b) polarity of the molecule or presence of strong polar groups even though the resultant dipole moment vanishes as in CO_2, SF_6

(c) large departures of shape from rough spherical symmetry as in the higher alkanes and alkenes.

The principle is not obeyed at all by substances whose molecules form hydrogen bonds, especially those containing hydroxyl or amino groups, nor those such as NO_2 whose molecules associate.

We shall now review briefly * some of the experimental data which show directly or indirectly how well certain substances especially Ne, A, Kr, Xe, N_2, O_2, CO, CH_4 obey an equation of state of the common form (1).

In table 4. 9 the first row gives the molar mass M, the next three rows the critical temperature T_c, critical volume V_c and critical pressure P_c. The fifth row gives values of $P_c V_c / R T_c$ which according to the principle should have a universal value. All the values lie close to 0.29. It is of interest to note that the value for xenon based on recent measurements is closer to 0.29 than the best experimental value 0.278 quoted in 1945.*

In fig. 4. 9 the experimental data on the second virial coefficients

* Guggenheim, *J. Chem. Phys.* 1945 **13** 253.
Cf. Pitzer, *J. Chem. Phys.* 1939 **7** 583.

TABLE 4. 9

Corresponding states of gases and liquids

	Formula	Ne	A	Kr	Xe	N_2	O_2	CO	CH_4
1	M/g mole^{-1}	20.18	39 94	83 7	131.3	28.02	32.00	28.00	16.03
2	T_c/°K	44.8	150 7	209.4	289 8	126.0	154.3	133.0	190.3
3	V_c/cm^3 mole^{-1}	41.7	75 3	92.1	118 8	90.2	74.5	93.2	98.8
4	P_c/atm	26.9	48 0	54 1	57.6	33.5	49.7	34.5	45.7
5	$P_c V_c/RT_c$	0 305	0 292	0.290	0.288	0.292	0 292	0.294	0.289
6	T_B/°K	121	411 5			327		~345	491
7	T_B/T_c	2.70	2.73			2.59		2 6	2.58
8	T_s/°K $(p = P_c/50)$	25.2	86.9	122 0	167.9	74.1	90.1	78.9	110.5
9	T_s/T_c	0.563	0.577	0 582	0.580	0.588	0.583	0.593	0.581
10	$\Delta_e H/R$°K	224	785	1086	1520	671	820	727	1023
11	$\Delta_e H/RT_s$	8.9	9.04	8 91	9 06	9 06	9.11	9 22	9.26
12	V_m/cm^3		28 1	34.1	42 7				
13	V_m/V_c		0 374	0.371	0.376				
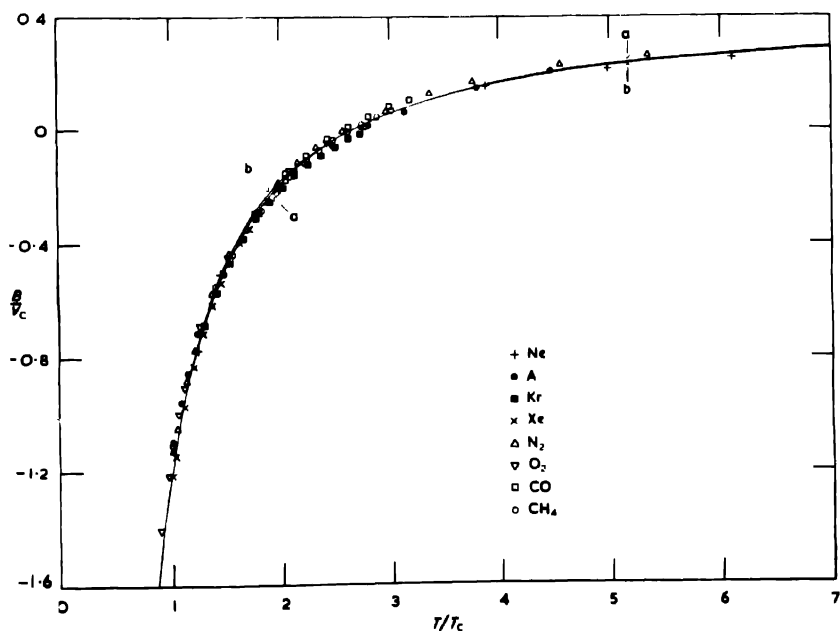
Fig. 4. 9. Second virial coefficients.

of these substances are shown in the form of B/V_c plotted against T/T_c. It will be seen that the data for the eight substances are well fitted by the same curve. The curve a in fig. 4. 9 represents the empirical formula

$$\frac{B}{V_c} = 0.438 - 0.881 \frac{T_c}{T} - 0.757 \frac{T_c^2}{T^2} \qquad 4.\,53.\,4$$

The curve b in fig. 4. 9 represents the formula

$$\frac{B}{V_c} = 0.447 \left\{ 3.375 - 2.375 \exp\left(0.936 \frac{T_c}{T}\right) \right\} \qquad 4.\,53.\,5$$

which can be derived theoretically from an interaction energy ε between a pair of molecules distant r apart of the "square-well" form given by

$$
\begin{aligned}
r &< D & \varepsilon &= +\infty \\
D &< r < 1.5\,D & \varepsilon &= -u \\
r &> 1.5\,D & \varepsilon &= 0 & 4.\,53.\,6
\end{aligned}
$$

when the parameters D and u have the values given by

$$\tfrac{2}{3}\pi L D^3 = 0.447\,V_c$$
$$u = 0.936\,kT_c \qquad 4.\,53.\,7$$

The Boyle temperature T_B at which the second virial coefficient changes sign is given in the sixth row of table 4. 9. In the seventh row are given values of T_B/T_c and all these values lie near 2.7.

If ϱ^L denotes the density of the liquid and ϱ^G that of the vapour in mutual equilibrium at the temperature T, while ϱ_c denotes the density at the critical point, then according to the principle of corresponding states we should expect ϱ^L/ϱ_c and ϱ^G/ϱ_c to be common functions of T/T_c. How nearly this is the case is shown in fig. 4. 10. The curve in the diagram is drawn according to the empirical formulae

$$\frac{\varrho^L + \varrho^G}{2\varrho_c} = 1 + \frac{3}{4}\left(1 - \frac{T}{T_c}\right) \qquad 4.\,53.\,8$$

$$\frac{\varrho^L - \varrho^G}{\varrho_c} = \frac{7}{2}\left(1 - \frac{T}{T_c}\right)^{\frac{1}{3}} \qquad 4.\,53.\,9$$

It is a pure accident that the data can be represented by formulae with such simple numerical coefficients. These formulae as displayed

above are of high relative accuracy, but if used to compute ϱ^G the percentage inaccuracy increases with decrease of temperature and
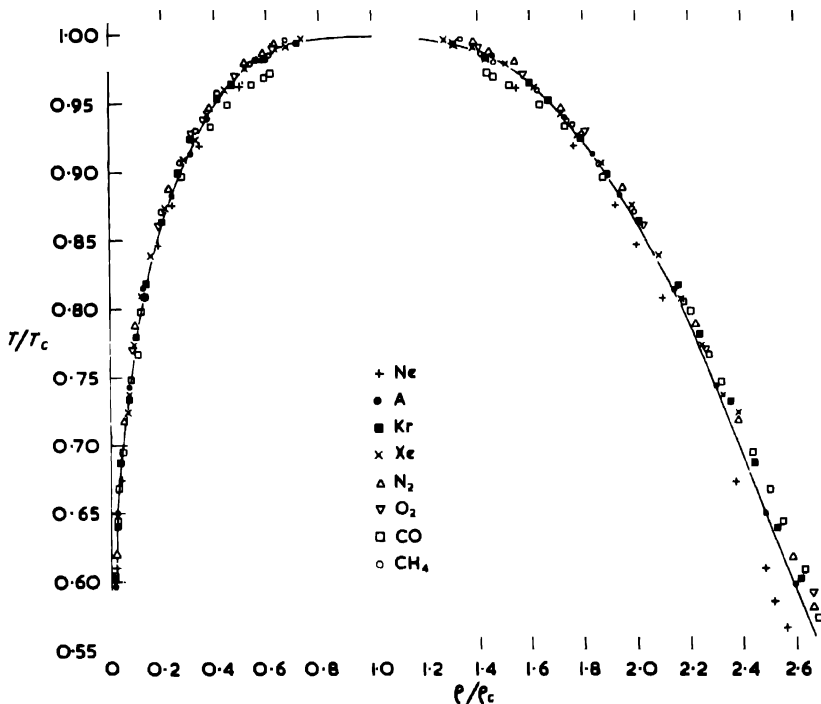
Fig. 4. 10. Reduced densities of coexisting liquid and gas phases.

becomes serious below $T \simeq 0.65\, T_c$. It is therefore not recommended to use these formulae for computing values of ϱ^G. There are however occasions when we require relatively accurate values, not of ϱ^G itself, but of $(\varrho^L - \varrho^G)/\varrho_c$; on such occasions formula (9), in view of its extreme simplicity and surprisingly high accuracy, has much to recommend it. An example of its use will occur in § 4. 74.

At temperatures considerably below the critical temperature, say $T < 0.65\, T_c$, it is more useful to consider the equilibrium vapour pressure p instead of ϱ^G. According to the principle of corresponding states we should expect p/P_c to be a common function of T/T_c. That this is approximately the case is seen from fig. 4. 11 where $\ln (p/P_c)$ is plotted against T_c/T for several substances. It is clear that the relation is nearly linear, so that we may write

$$\ln \frac{p}{P_c} = A \cdot B \frac{T_c}{T} \qquad 4.\,53.\,10$$

where A, B are constants having nearly the same values for the several substances. In the diagram the straight line which best fits the data for argon, krypton and xenon has been drawn. For this line

$$A = 5.29 \qquad B = 5.31 \qquad \text{(triple point to critical point)} \qquad 4.\,53.\,11$$

The fact that A is nearly but not exactly equal to B, means that the
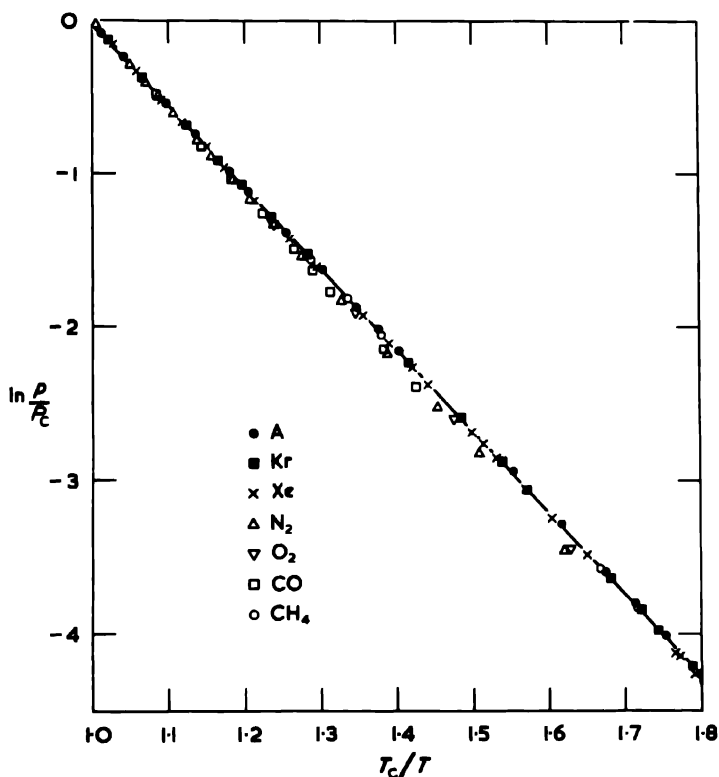
Fig. 4. 11. Relation between vapour pressure and temperature.

relation (11) holds nearly but not quite up to the critical temperature. A formula of the type (11) has a theoretical basis at low temperatures, where the vapour does not differ significantly from a perfect gas and the molar heat of evaporation is nearly independent of the temperature. Under these conditions $\Delta_e H/R = BT_c$. At higher temperatures where the vapour pressure is greater, neither of these conditions holds; the vapour deviates appreciably from a perfect gas and $\Delta_e H$ decreases, becoming zero at $T = T_c$. At such temperatures formula (11) is

empirical, but remains surprisingly accurate owing to a compensation between the two deviations.

In the temperature range between the triple point and the normal boiling point a formula of the type (11) becomes almost if not quite as accurate as the experimental data, but the best values for the constants A, B over this temperature range are not quite the same as the best values for the whole range from triple point to critical point. For argon an excellent fit of the experimental vapour pressures between the triple point and the normal boiling point and of the calorimetrically determined heat of evaporation is attained with the values

$$A = 5.13 \qquad B = 5.21 \qquad \text{(temperatures below n.b.p.)} \qquad 4.\,53.\,12$$

$$\frac{\Delta_e H}{R} = 5.21\, T_c \qquad\qquad 4.\,53.\,12$$

In the eighth row of table 4. 9 are given the temperatures T_s at which the vapour pressure has a value one fiftieth of the critical pressure. In the ninth row are given values of the ratio T_s/T_c. These are all close to 0.58.

In the tenth row of this table are given values of $\Delta_e H$ the molar heat of evaporation in the low temperature range where it is nearly independent of the temperature. In the eleventh column are given values of $\Delta_e H/R T_s$. All these values lie near to 9.0. Since $\Delta_e H/T$ is the entropy of evaporation, this aspect of the principle of corresponding states may be formulated thus: the entropy of evaporation at *corresponding temperatures*, e.g. temperatures at which the vapour pressure is one fiftieth the critical pressure, has a common value. The older rule of Trouton that substances should have the same entropy of evaporation at their *normal boiling points* is not in accord with the principle of corresponding states and is in somewhat less good agreement with the facts.

In the twelfth row of the table are given values of V_m the molar volume of the liquid at temperatures just above the triple point and in the thirteenth row values of the ratio V_m/V_c. These values are all near to 0.375.

§ 4. 54 CORRESPONDING STATES OF SOLIDS

The principle of corresponding states has a much more restricted applicability to solids. It however applies with high accuracy to the

group of the inert elements Ne, A, Kr, Xe. The relevant data for comparison are given in table 4. 10. In the first three rows are given values of T_c, V_c and P_c.

<div align="center">TABLE 4. 10</div>

<div align="center">Corresponding states of solids</div>

	Formula	Ne	A	Kr	Xe
1	$T_c/^\circ K$	44.8	150.7	209.4	289.8
2	$V_c/cm^3\ mole^{-1}$	41.7	75.3	92.1	118.8
3	P_c/atm	26 9	48.0	54.1	58.0
4	$T_t/^\circ K$	24 6	83 8	116.0	161.3
5	T_t/T_c	0 549	0.557	0.553	0.557
6	$\Delta_t H/R^\circ K$	40.3	141.3	196.2	276
7	$\Delta_t H/RT_t$	1.64	1.69	1.69	1 71
8	P_t/atm	0.425	0.682	0.721	0.810
9	$100\ P_t/P_c$	1 58	1.42	1 33	1.40
10	V^L/cm^3		28.14	34.13	42 68
11	V^S/cm^3		24.61	29.65	37.09
12	V^L/V^S		1.144	1.151	1 151

In the fourth row are given values of the triple point temperature T_t and in the fifth row values of the ratio T_t/T_c. All these values are near to 0.555.

In the sixth row are given values of the molar heat of fusion $\Delta_t H$ divided by R and in the seventh row values of the entropy of fusion $\Delta_t H/T_t$ divided by R. These are all near to 1.69.

In the eighth row are given values of P_t the triple point pressure and in the ninth row values of the ratio $100\ P_t/P_c$. These are all near to 1.4.

Finally in the tenth and eleventh rows are given the molar volumes V^L and V^S of the liquid and solid respectively both at the triple point. In the twelfth row are given the ratios V^L/V^S, all near to 1.15.

§ 4. 55 ENERGY AND ENTROPY CONSTANTS

In § 4. 16 and §§ 4. 29—4. 33 we discussed in some detail the thermodynamic functions of gases. As well as directly measurable quantities such as T, P, B and certain characteristic temperatures Θ_r, Θ_v, Θ_e all well defined properties of the molecules, these formulae contained two

further constants H^0 and $\Theta^\dagger$ which we have as yet hardly discussed at all. To be precise the molar heat function H_m contains the additive constant H^0, which we shall now write as $H_m^G(0)$ to show that it refers to the gas phase, while the molar entropy S_m contains the additive constant $-\frac{5}{2}R\ln\Theta^\dagger$. The chemical potential μ consequently involves both these constants.

In § 4. 36 we described the behaviour of the thermodynamic functions of a crystal at very low temperatures. We saw that the molar heat content H_m contains an additive constant H_m^0, which we shall now write as $H_{\tilde{m}}^S(0)$ to contrast it with $H_m^G(0)$. Similarly the molar entropy contained an additive constant $S_{\tilde{m}}^0$. It will be convenient to define a number o by the relation

$$S_{\tilde{m}}^0 = R\ln o \qquad\qquad 4.\,55.\,1$$

The chemical potential of a crystal consequently involves both the constants $H_{\tilde{m}}^S(0)$ and $S_{\tilde{m}}^0$ or o.

As long as we are concerned only with one single phase, the relevant constants are without any physical significance. It is when we come to compare two phases, that we must be careful to assign values to the constants corresponding to the same conventions.

As regards the heat function constants $H_m^G(0)$ and $H_{\tilde{m}}^S(0)$ there is little to be said except that when referred to the same energy zero, as they must be if we wish to compare them at all, $H_m^G(0) - H_{\tilde{m}}^S(0)$ is the value of the molar heat of sublimation of the crystal extrapolated to the absolute zero of temperature. If the heat of sublimation $\Delta_s H$ has been measured at the temperature T, we have

$$\Delta_s H(T) = H_m^G(T) - H_{\tilde{m}}^S(T) \qquad\qquad 4.\,55.\,2$$

Direct calorimetric measurements on the crystal lead to an experimental value of

$$H_{\tilde{m}}^S(T) - H_{\tilde{m}}^S(T_0) \qquad\qquad 4.\,55.\,3$$

where T_0 is some very low temperature. A short extrapolation, according to formula (4. 36. 1) leads to a value of

$$H_{\tilde{m}}^S(T) - H_{\tilde{m}}^S(0) \qquad\qquad 4.\,55.\,4$$

Theoretical information concerning the nature of the gaseous molecules, or alternatively calorimetric measurements together with an extra-

polation to $T = 0$ in accordance with the theory of the various types of gaseous molecules, gives a value of

$$H_m^G (T) — H_m^G (0) \qquad 4.\,55.\,5$$

By adding the quantities (2) and (4) and subtracting the quantity (5) we can obtain the value of

$$H_m^G (0) — H_m^S (0) \qquad 4.\,55.\,6$$

We turn now to the more interesting entropy constants — $\frac{5}{2}R \ln \Theta^\dagger$ and $R \ln o$. We described in detail in § 4.04 how to determine experimentally the entropy difference between any two states of a single substance. In particular we can determine experimentally the value of

$$S_m^G (T) — S_m^S (T_0) \qquad 4.\,55.\,7$$

where T_0 is some very low temperature. Extrapolating to $T_0 \rightarrow 0$ in accordance with (4.36.2) we obtain an experimental value of

$$S_m^G (T) — S_m^S (0) = S_m^G (T) — R \ln o \qquad 4.\,55.\,8$$

Knowing the values of all the terms in $S_m^G (T)$ except the constant — $\frac{5}{2}R \ln \Theta^\dagger$ we thus obtain an experimental value of

$$R \ln (\Theta^{\dagger\frac{5}{2}} o) \qquad 4.\,55.\,9$$

This quantity will be discussed in the following sections.

§ 4.56 ENTROPY CONSTANTS OF MONATOMIC SUBSTANCES

We begin by considering monatomic substances, since such complications as occasionally occur for other types of molecules are entirely absent for these. We shall discuss in turn the possible contributions of the various degrees of freedom to the quantity (4.55.8) namely

$$R \ln (\Theta^{\dagger\frac{5}{2}} o) \qquad 4.\,56.\,1$$

Firstly as regards any intranuclear degrees of freedom, in particular that due to nuclear spin, their contributions to the solid and to the gas are the same and consequently they make no contribution to (1).

Secondly as regards the electronic degrees of freedom, any contribution in the gaseous state has been allowed for as described in § 4.33 and is not contained in the $\Theta^\dagger$ term. In the solid at low temperatures we may safely assert that there is no electronic contribution.

There remain only the translational degrees of freedom. In the solid these account for the terms which are represented approximately by the temperature dependent terms in Debye's formulae. At very low

temperatures they are adequately represented by the term $\frac{4}{3}aT^3$ in (4. 36. 2) and they tend to zero as $T \to 0$. Consequently they contribute nothing to (1). There remains only the contribution of the translational degrees of freedom in the gas and by comparing the statistical formula (2. 17. 7) with the classical formula (4. 29. 4) we obtain

$$\Theta^{\dagger\frac{5}{2}} o = \frac{h^3 P^\dagger}{(2\pi m)^{\frac{3}{2}} k^{\frac{5}{2}}} \qquad\qquad 4. 56. 2$$

where h is Planck's constant, k is Boltzmann's constant, m is the mass of one molecule (atom) and $P^\dagger$ is the arbitrary standard pressure occurring in the formulae of § 4. 29. Obviously $\Theta^\dagger$ must depend on $P^\dagger$ in such a manner that the value of any thermodynamic function at a given pressure P is independent of the arbitrary choice of $P^\dagger$.

For a substance which in the gaseous state has monatomic molecules formula (2) is generally valid and is independent of any conventional zero of entropy. We now replace the invariant relation (2) by the conventional pair of relations

$$\Theta^{\dagger\frac{5}{2}} = \frac{h^3 P^\dagger}{(2\pi m)^{\frac{3}{2}} k^{\frac{5}{2}}} \qquad\qquad 4. 56. 3$$

$$o = 1 \qquad\qquad 4. 56. 4$$

Formula (4) is equivalent to the convention

$$S_m^S (0) = 0 \qquad\qquad 4. 56. 5$$

These formulae correspond to the following conventional definition of zero entropy. The entropy of a monatomic substance is conventionally defined to be zero in a state such that

(a)   the contributions to the entropy from the translational and electronic degrees of freedom are zero;

(b)   the contributions from any intranuclear degrees of freedom including spin are ignored, this being allowable only because the contributions are, under terrestrial conditions, independent of temperature and of the state of the substance.

This conventional choice of zero entropy has proved convenient and is widely used. Some authors use the expression *absolute entropy* to denote the value of the entropy according to the convention (5) or some closely related convention. Such terminology may be misleading

and should be avoided. The only rational system of entropies to which one might reasonably apply the epithet *absolute* would be one referred to certain standard states of the fundamental particles, protons, neutrons and electrons of which matter consists. It is hardly necessary to state that the use of such a system is not at present feasible owing to lack of data on the entropy changes associated with nuclear transmutations. Even if feasible, it is doubtful whether it would serve any useful purpose in the field of terrestial physics and chemistry.

To recapitulate, the convention (5) is, at least for terrestial conditions, the most convenient, but it is in no sense absolute. We shall accordingly refer to the entropy values conforming to the convention (5) as the *conventional entropy values*.

§ 4. 57 EFFECT OF ISOTOPES

In the previous section we tacitly ignored any possible effect due to the substance being a mixture of isotopes. When this is the case there are two possible effects on the entropy. The first effect is the obvious one that the term $\frac{3}{2}R \ln m$ in the entropy must be replaced by the suitably weighted sum

$$\frac{3}{2}R \, \Sigma_i \, x_i \ln m_i \qquad\qquad 4.\,57.\,1$$

where x_i is the mole fraction of the particular isotope i having an atomic mass m_i. Similarly the constant $H_m^G(0)$ occurring in H_m and in μ, but not in S_m, must be replaced by the weighted sum

$$\Sigma_i \, x_i \, H_i^G(0) \qquad\qquad 4.\,57.\,2$$

The second effect is that any phase, whether solid, liquid or gaseous consisting of a mixture of isotopes in mole fractions x_i has an entropy per mole exceeding the entropy per mole of similar phases of the pure isotopes at the same temperature and pressure and this excess is

$$- R \, \Sigma_i \, x_i \ln x_i \qquad\qquad 4.\,57.\,3$$

which is always a positive quantity since $x_i < 1$.

We shall meet formula (3) for *entropies of mixing* again in chapter 5. In the present connection we need only note that as long as the solid and the gas have the same isotopic composition, the two terms of the form (3) cancel and so contribute nothing to Θ†.

§ 4. 58 NUMERICAL VALUES IN ENTROPY CONSTANT

We shall now insert numerical values into (4. 56. 3), taking as our standard pressure $P^\dagger = 1$ atmosphere. We have then

$$h = 6.625 \times 10^{-27} \text{ erg s}$$
$$k = 1.3803 \times 10^{-16} \text{ erg deg}^{-1}$$
$$P^\dagger = 1.0132 \times 10^6 \text{ erg cm}^{-3}$$
$$m = \frac{M}{\text{g mole}^{-1}} \times 1.660 \times 10^{-24} \text{ g}$$

where M is the molar mass. Using these values we obtain

$$\Theta^{\dagger \frac{5}{2}} \left(\frac{M}{\text{g mole}^{-1}} \right)^{\frac{3}{2}} = 39.07 \text{ deg}^{\frac{5}{2}} = (4.33_3 \text{ deg})^{\frac{5}{2}} \quad (P^\dagger = 1 \text{ atm}) \quad 4.\,58.\,1$$

Inserting this in formulae (4. 29. 2), (4. 29. 3) and (4. 29. 4), we obtain *

$$\ln \lambda^\dagger = \frac{\mu^\dagger}{RT} = \frac{H^0}{RT} - \tfrac{5}{2} \ln \frac{T}{4.33_3 \text{ deg}} - \tfrac{3}{2} \ln \frac{M}{\text{g mole}^{-1}} \quad (P^\dagger = 1 \text{ atm})$$
$$4.\,58.\,2$$

$$\ln \lambda = \frac{\mu}{RT} = \frac{H^0}{RT} - \tfrac{5}{2} \ln \frac{T}{4.33_3 \text{ deg}} - \tfrac{3}{2} \ln \frac{M}{\text{g mole}^{-1}} + \ln \frac{P}{\text{atm}} + \frac{PB}{RT}$$
$$4.\,58.\,3$$

$$\frac{S_m}{R} = \tfrac{3}{2} + \tfrac{5}{2} \ln \frac{T}{4.33_3 \text{ deg}} + \tfrac{3}{2} \ln \frac{M}{\text{g mole}^{-1}} - \ln \frac{P}{\text{atm}} - \frac{P}{R} \frac{dB}{dT}$$

$$= \tfrac{5}{2} \ln \frac{T}{1.59_4 \text{ deg}} + \tfrac{3}{2} \ln \frac{M}{\text{g mole}^{-1}} - \ln \frac{P}{\text{atm}} - \frac{P}{R} \frac{dB}{dT} \quad 4.\,58.\,4$$

Formula (4) can also be written as

$$\frac{S_m}{R} = -1.16_6 + \tfrac{3}{2} \ln \frac{M}{\text{g mole}^{-1}} + \tfrac{5}{2} \ln \frac{T}{\text{deg}} - \ln \frac{P}{\text{atm}} - \frac{P}{R} \frac{dB}{dT}$$
$$4.\,58.\,5$$

or more conveniently as

$$\frac{S_m}{R} = 10.35 + \tfrac{3}{2} \ln \frac{M}{\text{g mole}^{-1}} + \tfrac{5}{2} \ln \frac{T}{100 \text{ deg}} - \ln \frac{P}{\text{atm}} - \frac{P}{R} \frac{dB}{dT}$$
$$4.\,58.\,6$$

* We recall that H^0 is the same quantity as is denoted by $H^0_m(0)$ in § 4. 55.

The corresponding formulae for μ/RT are

$$\frac{\mu}{RT} = \frac{H^0}{RT} + 3.66_6 - \tfrac{3}{2}\ln\frac{M}{\text{g mole}^{-1}} - \tfrac{5}{2}\ln\frac{T}{\deg} + \ln\frac{P}{\text{atm}} + \frac{PB}{RT}$$

4. 58. 7

$$\frac{\mu}{RT} = \frac{H^0}{RT} - 7.85 - \tfrac{3}{2}\ln\frac{M}{\text{g mole}^{-1}} - \tfrac{5}{2}\ln\frac{T}{100\ \deg} + \ln\frac{P}{\text{atm}} + \frac{PB}{RT}$$

4. 58. 8

Formulae (6) and (8) are of a form such that the numerical calculations can be completed with adequate accuracy by slide-rule.

§ 4. 59 ENTROPY CONSTANTS OF DIATOMIC AND POLYATOMIC SUBSTANCES

As explained in § 4. 55 calorimetric measurements yield experimental values of

$$R \ln \left(\Theta^{\dagger\frac{5}{2}} o\right)$$

4. 59. 1

Just as for substances with monatomic molecules we continue to assume that

$$\Theta^{\dagger\frac{5}{2}} = \frac{h^3 P^\dagger}{(2\pi m)^{\frac{3}{2}} k^{\frac{5}{2}}}$$

4. 59. 2

precisely as in (4. 56. 3). This corresponds to a conventional definition of zero entropy which includes our previous convention for monatomic molecules as a special case. This conventional choice of states of zero entropy is the following:

(a) the contributions to the entropy from the translational and electronic degrees of freedom are zero;

(a') the contributions to the entropy from the rotational and internal vibrational degrees of freedom are zero;

(b) the contributions due to any intranuclear degrees of freedom including spin are ignored, this being allowable only because the contributions are, under terrestrial conditions, independent of temperature and of the state of the substance;

(c) isotopic composition is ignored, this being allowable in so far as it is the same in all phases being compared.

For monatomic molecules the conditions (a') were automatically satisfied and were therefore not mentioned. In the case of hydrogen

the assumption (*b*) is subject to certain restrictions which we shall consider in § 4. 64.

Precisely as in the case of monatomic molecules, the convention described is convenient and generally used. We shall refer to entropy values thus fixed as *conventional entropy values* and shall avoid the misleading expression *absolute entropy*.

Applying the convention (2) to the experimental values of (1), we obtain conventional values of *o* which we shall discuss in the next section.

§ 4. 60 ZERO-ENTROPIES OF CRYSTALS

It is found that the conventional values of *o* obtained as described in the preceding section are in almost all cases unity but that there are exceptions. We shall consider first the physical meaning of

$$o = 1 \qquad\qquad 4.\ 60.\ 1$$

and then the physical meaning of the exceptions.

We recall that *o* was defined by (4. 55. 1)

$$S_m^0 = R \ln o \qquad\qquad 4.\ 60.\ 2$$

and that S_m^0 is obtained from experimental values of S at low temperatures by extrapolation according to (4. 36. 2). Provided the experimental data reach down to below 20 °K, the term

$$S_m(T) - S_m^0 = \tfrac{1}{3}aT^3 \qquad\qquad 4.\ 60.\ 3$$

is so small that no appreciable error arises either from an error in the precise form of the relation assumed between S and T or from an inaccurate value of *a*. There is however a far more serious hidden assumption implied in the extrapolation, namely that the relation (3) does not completely break down at some temperature below that to which the experimental data extend. Owing to the possibility of this occurrence and the impossibility of a complete experimental disproof, it is well to remember that S_m^0, which we shall call the *zero-entropy* of the crystal, is the entropy smoothly *extrapolated to $T = 0$* and is not necessarily the entropy *at $T = 0$*. Whereas obviously there is at any given date no experimental answer as to what happens in the temperature range still inaccessible to experiment, statistical theory can tell us when, if ever, it is reasonable to expect complications of the kind described. It in fact tells us that in most cases it is reasonably safe to

assume that such possible complications are absent. It also tells us where to expect exceptions. One important exception, namely hydrogen, will be discussed in § 4. 64.

The condition $o = 1$ found for most crystals means that the conventional zero-entropy of the crystal is zero. According to the convention chosen in § 4. 59 this means that the contributions to the entropy from the translational, electronic, rotational and internal vibrational degrees of freedom are all zero. In other words disregarding intranuclear degrees of freedom and isotopic composition, we may say that no other degrees of freedom contribute anything to the entropy. Statistical theory tells us that this corresponds to the crystal being in a perfectly ordered state, provided we disregard intranuclear degrees of freedom and isotopic composition. Thus a combination of statistical theory with experimental data tells us that as the temperature decreases, most crystals tend towards a state of perfect order apart from intranuclear phenomena and isotopic composition. More strictly we should say that this is how the crystal appears to behave judged by the experimental data in the region of 20 °K.

§ 4. 61 SIMPLE TYPICAL EXCEPTIONS

We shall now consider exceptions to the general rule $o = 1$. The two simplest are CO and NNO. In both cases the experimental evidence is that $o > 1$ and within the experimental accuracy $o = 2$. The statistical interpretation of a value 2 for o, is that instead of perfect order in the crystal, there are two possible orientations for each molecule and the molecules are randomly distributed between these two orientations. This is what we should expect to happen in the case of a linear molecule whose field of force is nearly but not quite symmetrical so that the molecule can be reversed end for end without an appreciable energy change. Statistical theory tells us that the equilibrium distribution of directions will remain random down to temperatures at which kT is comparable with the energy difference in the two orientations. At temperatures where kT is much smaller than the energy difference between the two orientations, then only one orientation will be stable, but at such low temperatures it may well be that the molecules have not sufficient energy to turn round. In simple words when the crystal is so cold that the molecules have a preference for one orientation they have too little energy (are "too cold") to change their orientations. Such a crystal at the lowest temperatures will remain in a state with $o = 2$ and this state is metastable with respect to the ideal unrealizable state of

ordered orientation with $o = 1$. It is believed that this is a true description of the behaviour of crystalline CO and NNO at the lowest temperatures. It is interesting to note that the SCO molecule is not sufficiently symmetrical to behave in this way and the experimental data are consistent with $o = 1$.

The case of NO is somewhat more complicated. It is suggested that at the lowest temperatures the molecular unit is $\begin{smallmatrix} N & O \\ O & N \end{smallmatrix}$ and that owing to the similarity between N and O atoms the two orientations $\begin{smallmatrix} N & O \\ O & N \end{smallmatrix}$ and $\begin{smallmatrix} O & N \\ N & O \end{smallmatrix}$ have nearly equal energies. There would then be a random distribution over these two orientations. This would lead to a value of $o = 2$ for the molecular unit N_2O_2; the corresponding value of o expressed in terms of the molecule NO is $2^{\frac{1}{2}}$ and this value is in agreement with experiment within the estimated accuracy.

The other well established case of $o > 1$ believed due to simple orientational randomness is that of ice. To account for the experimental data the following assumptions are made.

(1) In ice each oxygen atom has two hydrogens attached to it at distances about 0.95 Å forming a molecule, the HOH angle being about 105° as in the gas molecule.

(2) Each HOH molecule is oriented so that its two H atoms are directed approximately towards two of the four O atoms which surround it tetrahedrally.

(3) The orientations of adjacent HOH molecules are such that only one H atom lies approximately along each O—O axis.

(4) Under ordinary conditions the interaction of non-adjacent molecules is not such as to stabilize appreciably any one of the many configurations satisfying the preceding conditions relative to the others.

On these assumptions Pauling * calculated that theoretically $o = \frac{3}{2}$. Experimentally this value is verified for both H_2O and D_2O.

§ 4. 62 NUMERICAL VALUES IN FORMULAE FOR LINEAR MOLECULES

For linear molecules, including diatomic molecules, the formula for $\mu^\dagger$ is the same as (4. 58. 2) for monatomic molecules. When we substitute this into the formulae of § 4. 31 we obtain

* Pauling, *J. Amer. Chem. Soc.* 1935 **57** 2680

$$\ln \lambda = \frac{\mu}{RT} = \frac{H^0}{RT} - \tfrac{5}{2} \ln \frac{T}{4.33_3 \, \text{deg}} - \tfrac{3}{2} \ln \frac{M}{\text{g mole}^{-1}} - \ln \frac{T}{\Theta_r \sigma}$$

$$+ \sum_{\Theta_v} \ln \left(1 - e^{-\Theta_v/T}\right) + \ln \frac{P}{\text{atm}} + \frac{PB}{RT} \qquad \text{4. 62. 1}$$

$$\frac{S_m}{R} = \tfrac{7}{2} + \tfrac{5}{2} \ln \frac{T}{4.33_3 \, \text{deg}} + \tfrac{3}{2} \ln \frac{M}{\text{g mole}^{-1}} + \ln \frac{T}{\Theta_r \sigma}$$

$$- \sum_{\Theta_v} \ln \left(1 - e^{-\Theta_v/T}\right) + \sum_{\Theta_v} \frac{\Theta_v/T}{e^{\Theta_v/T} - 1} - \ln \frac{P}{\text{atm}} - \frac{P}{R} \frac{dB}{dT}$$

$$= \tfrac{5}{2} \ln \frac{T}{1.06_9 \, \text{deg}} + \tfrac{3}{2} \ln \frac{M}{\text{g mole}^{-1}} + \ln \frac{T}{\Theta_r \sigma} - \sum_{\Theta_v} \ln \left(1 - e^{-\Theta_v/T}\right)$$

$$+ \sum_{\Theta_v} \frac{\Theta_v/T}{e^{\Theta_v/T} - 1} - \ln \frac{P}{\text{atm}} - \frac{P}{R} \frac{dB}{dT} \qquad \text{4. 62. 2}$$

For diatomic molecules each Σ reduces to a single term.

§ 4. 63 NUMERICAL VALUES IN FORMULAE FOR NON-LINEAR MOLECULES

For polyatomic non-linear molecules the formula (4. 58. 2) for $\mu^\dagger$ still holds. When we substitute this into the formulae of § 4. 32, we obtain

$$\ln \lambda = \frac{\mu}{RT} = \frac{H^0}{RT} - \tfrac{5}{2} \ln \frac{T}{4.33_3 \, \text{deg}} - \tfrac{3}{2} \ln \frac{M}{\text{g mole}^{-1}} - \ln \frac{\pi^{\frac{1}{2}} T^{\frac{3}{2}}}{\Theta_r^{\frac{3}{2}} \sigma}$$

$$+ \sum_{\Theta_v} \ln \left(1 - e^{-\Theta_v/T}\right) + \ln \frac{P}{\text{atm}} + \frac{PB}{RT} \qquad \text{4. 63. 1}$$

$$\frac{S_m}{R} = 4 + \tfrac{5}{2} \ln \frac{T}{4.33_3 \, \text{deg}} + \tfrac{3}{2} \ln \frac{M}{\text{g mole}^{-1}} + \ln \frac{\pi^{\frac{1}{2}} T^{\frac{3}{2}}}{\Theta_r^{\frac{3}{2}} \sigma}$$

$$- \sum_{\Theta_v} \ln \left(1 - e^{-\Theta_v/T}\right) + \sum_{\Theta_v} \frac{\Theta_v/T}{e^{\Theta_v/T} - 1} - \ln \frac{P}{\text{atm}} - \frac{P}{R} \frac{dB}{dT}$$

$$\tfrac{5}{2} \ln \frac{T}{0.696_4 \, \text{deg}} + \tfrac{3}{2} \ln \frac{M}{\text{g mole}^{-1}} + \ln \frac{T^{\frac{3}{2}}}{\Theta_r^{\frac{3}{2}} \sigma} - \sum_{\Theta_v} \ln \left(1 - e^{-\Theta_v/T}\right)$$

$$+ \sum_{\Theta_v} \frac{\Theta_v/T}{e^{\Theta_v/T} - 1} - \ln \frac{P}{\text{atm}} - \frac{P}{R} \frac{dB}{dT} \qquad \text{4. 63. 2}$$

As an example of the use of these formulae let us calculate the molar entropy of steam at a temperature 373.15 °K and a pressure of one atmosphere. For water $M = 18.02$ g mole^{-1} and so

$$4 + \tfrac{5}{2} \ln \frac{T}{4.33_3 \text{ deg}} + \tfrac{1}{2} \ln \frac{M}{\text{g mole}^{-1}} = 4 + \tfrac{5}{2} \ln \frac{373.15}{4.33_3} + \tfrac{1}{2} \ln 18.02$$

$$= 4 + 11.14 + 4.34 = 19.48$$

The rotational characteristic temperature of OH_2 is $\Theta_r = 22.3$ deg and the symmetry number is $\sigma = 2$, so that

$$\ln \frac{\pi^{\frac{1}{2}} T^{\frac{3}{2}}}{\Theta_r^{\frac{3}{2}} \sigma} = \ln \left\{ \frac{\pi^{\frac{1}{2}}}{2} \left(\frac{373.15}{22.3} \right)^{\frac{3}{2}} \right\} = 4.11$$

The vibrational characteristic temperatures Θ_v are $2290°$, $5250°$ and $5400°$. For the contribution of the first we have

$$- \ln \left(1 - e^{-2290/373} \right) + \frac{2290/373}{e^{2290/373} - 1} = 0.002 + 0.014 = 0.02$$

The contributions from the other two frequencies are negligible.

Since we are interested in the entropy at a pressure of one atmosphere, we have

$$- \ln \frac{P}{\text{atm}} = 0$$

The correction term involving the second virial coefficient is negligible. Adding the several contributions we obtain

$$\frac{S_m}{R} = 19.48 + 4.11 + 0.02 = 23.61$$

$$(T = 373.15 \text{ °K}, \quad P = 1 \text{ atm}) \qquad 4.\,63.\,3$$

Let us now compare this with the experimental value of $(S_m - S_m^0)/R$ determined calorimetrically. From the calculation made in § 4.04 we have

$$S_m^G (373.15 \text{ °K, 1 atm}) - S_m^S (0)$$

$$= (38.09 + 21.99 + 23.52 + 108.95) \text{ J deg}^{-1} \text{ mole}^{-1}$$

$$= 192.55 \text{ J deg}^{-1} \text{ mole}^{-1}$$

and dividing by $R = 8.3147$ J deg^{-1} mole^{-1}

$$\frac{S_m^G \ (373.15 \ °K) - S_m^S \ (0)}{R} = \frac{192.55}{8.3147} = 23.16 \qquad 4.\ 63.\ 4$$

Subtracting (4) from (3) we obtain

$$S_m^S \ (0)/R = S_m^0/R = \ln o = 0.45 \qquad 4.\ 63.\ 5$$

in good agreement with Pauling's theoretical value discussed at the end of § 4. 6]

$$\ln o = \ln \tfrac{1}{2} = 0.41. \qquad 4.\ 63.\ 6$$

§ 4. 64 THE EXCEPTIONAL CASE OF HYDROGEN

Hydrogen is exceptional in several respects. This is due partly to its molecule having such a small moment of inertia with a consequently high value of the rotational characteristic temperature $\Theta_r = 85.4°$. It is also partly due to the molecule's having an exceptionally small field of force so that even at very low temperatures it still rotates in the crystal. We shall not here go into the theory * of the behaviour of hydrogen as this would take us too far afield. We shall merely state the facts sufficiently to show how the various thermodynamic formulae must be used so as to obtain correct results.

For the sake of consistency we define our conventional zero of entropy precisely as for all other molecules, so that formula (4. 59. 2) is valid for the gas. As regards the physical meaning of this convention the statements (a), (a') and (c) of § 4. 59 hold without any alteration, but statement (b) should be modified as follows:

(b)   the contributions due to any intranuclear degrees of freedom other than resultant nuclear spin are ignored and the contribution due to the spin of the two nuclei in a hydrogen molecule is taken to be the same as if the nuclei were present in independent atoms. Any actual deviation from this will then appear in o.

We shall first consider the gas. The usual formulae for gases with diatomic molecules are applicable only at temperatures large compared with Θ_r and consequently for H_2 they are valid only above about 300 °K.

As the temperature decreases from 300 °K to about 45 °K, the temperature dependent term in the molar heat function H_m decreases from the usual value $\tfrac{7}{2}RT$ for a diatomic gas to the value $\tfrac{5}{2}RT$ usually associated with a monatomic gas. At the same time the conventional

* Fowler and Guggenheim, *Statistical Thermodynamics* 1939 § 531.

molar entropy decreases from the usual form for a diatomic gas to a value which except for a constant term recalls that of a monatomic gas. To be precise

$$\frac{\mu}{RT} = \frac{H^0}{RT} - \tfrac{5}{2} \ln \frac{T}{\Theta\dagger} - \tfrac{3}{4} \ln 3 + \ln \frac{P}{P\dagger} + \frac{PB}{RT} \quad (T < 45\ ^\circ K) \quad 4.\ 64.\ 1$$

$$\frac{S_m}{R} = \tfrac{5}{2} + \tfrac{3}{2} \ln \frac{T}{\Theta\dagger} + \tfrac{1}{4} \ln 3 - \ln \frac{P}{P\dagger} - \frac{P}{R} \frac{dB}{dT} \quad (T < 45\ ^\circ K) \quad 4.\ 64.\ 2$$

$$\frac{H_m}{RT} = \frac{H^0}{RT} + \tfrac{5}{2} + \frac{P}{R}\left(B - T\frac{dB}{dT}\right) \quad\quad (T < 45\ ^\circ K) \quad 4.\ 64.\ 3$$

The constant term $\tfrac{3}{4} \ln 3$ in (2) is due to the fact that hydrogen behaves as a mixture of $\tfrac{1}{4}$ para hydrogen with a molar rotational entropy zero at low temperatures and $\tfrac{3}{4}$ ortho hydrogen with a molar rotational entropy $R \ln 3$ at low temperatures.

Turning now to the crystal, let us first ignore any experimental data below 12 °K and extrapolate smoothly the data between 20 °K and 12 °K in the usual way. We thus obtain well determined values of

$$S_m^G (T) - S_m^S (0) = S_m^G (T) - R \ln o \quad\quad 4.\ 64.\ 4$$

We may use the usual formula for $S_m^G (T)$ with $T > 300$ °K or alternatively formula (2) for $S_m^G (T)$ with $T < 45$ °K; by either procedure we obtain a value for o agreeing within the experimental error with

$$\ln o = \tfrac{3}{4} \ln 3 \quad\quad 4.\ 64.\ 5$$

We notice that the conventional zero-entropy of the crystal obtained by smooth extrapolation from 12 °K is the same as the conventional entropy in the gas below 45 °K.

This would complete the picture of ordinary hydrogen were it not for the existence of experimental data on the crystal between 12 °K and 2 °K. In this range the entropy decreases with anomalous rapidity. In fact the heat capacity not only is anomalously greater than corresponds to the form aT^3, but it actually increases as the temperature decreases below 6 °K. On theoretical grounds it is clear that the orthomolecules are somehow beginning to "line up" with a consequent decrease of entropy. There can be little doubt that if these experimental data extended to still lower temperatures the heat capacity would eventually become normal again after there had been a total loss of

molar entropy $\frac{3}{4}R \ln 3$. If we then determined $S_m^S(0)$ from here instead of by extrapolation from 12 °K, we should find

$$o = 1 \qquad\qquad 4.\,64.\,6$$

Up to this point we have assumed that the crystal, like the gas, consists of the ordinary metastable mixture of $\frac{1}{4}$ para hydrogen and $\frac{3}{4}$ ortho hydrogen. For this mixture the contributions of nuclear spin to the entropy are normal and so their conventional omission leads to no complications. If however the crystalline hydrogen were converted to stable pure para hydrogen there would be a decrease in the contributions to the molar entropy, from the nuclear spins and from the mixing of the para and orthomolecules, from $R \ln 4$ to $R \ln 1$, which would manifest itself as

$$o = \frac{1}{4} \qquad\qquad 4.\,64.\,7$$

The conventional zero-entropy of stable para hydrogen has the negative value

$$S_m^0 = - R \ln 4 \qquad \text{(para hydrogen)} \qquad 4.\,64.\,8$$

For deuterium D_2 the general picture is similar with several differences of detail. The gas behaves like other diatomic gases at temperatures exceeding 200 °K. Between this temperature and about 25 °K, the temperature dependent term in the molar heat function H_m decreases to the value $\frac{5}{2}RT$ usually associated with a monatomic gas and there is of course a corresponding drop in the molar entropy. To be precise

$$\frac{\mu}{RT} = \frac{H^0}{RT} - \tfrac{5}{2} \ln \frac{T}{\Theta^\dagger} - \tfrac{1}{3} \ln 3 + \ln \frac{P}{P^\dagger} + \frac{PB}{RT} \quad (T < 25\ ^\circ\text{K}) \quad 4.\,64.\,9$$

$$\frac{S_m}{R} = \tfrac{5}{2} + \tfrac{5}{2} \ln \frac{T}{\Theta^\dagger} + \tfrac{1}{3} \ln 3 - \ln \frac{P}{P^\dagger} - \frac{P}{R}\frac{dB}{dT} \quad (T < 25\ ^\circ\text{K}) \quad 4.\,64.\,10$$

$$\frac{H_m}{RT} = \frac{H^0}{RT} + \tfrac{5}{2} + \frac{P}{R}\left(B - T\frac{dB}{dT}\right) \qquad (T < 25\ ^\circ\text{K}) \quad 4.\,64.\,11$$

The constant term $\frac{1}{3} \ln 3$ in (10) is due to the fact that D_2 behaves as a mixture of $\frac{2}{3}$ ortho deuterium with a molar rotational entropy zero at low temperatures and $\frac{1}{3}$ para deuterium with a molar rotational entropy $R \ln 3$ at low temperatures.

For the crystal similarly, if one extrapolates in the usual way from a temperature between 20 °K and 10 °K one obtains

$$S_m^S(0)/R = S_m^0/R = \ln o = \tfrac{1}{3} \ln 3 \qquad\qquad 4.\,64\ \ 12$$

There are as yet no experimental data at low enough temperatures to show the disappearance of this entropy.

For the ordinary metastable mixture of $\frac{2}{3}$ ortho deuterium and $\frac{1}{3}$ para deuterium, the contributions of nuclear spin to the entropy are normal and so their conventional omission leads to no complications. When however the crystalline deuterium is converted to stable pure ortho deuterium there is a decrease in the contributions to the molar entropy of the nuclear spins and the mixing of the ortho and para molecules from $R \ln 9$ to $R \ln 6$. If we assume that at the lowest temperatures the molecules line up, as we know to be the case with H_2, this will manifest itself as

$$o = \tfrac{6}{9} = \tfrac{2}{3} \qquad\qquad 4.\,64.\,13$$

The conventional zero-entropy of stable ortho deuterium is

$$S_m^0 = R \ln \tfrac{2}{3} \qquad\qquad 4.\,64.\,14$$

which is thus negative.

§ 4. 65 EFFECT OF ISOTOPES

In § 4. 57 we considered two possible effects due to the presence of isotopes in a monatomic substance. In the case of a diatomic or polyatomic substance there are three possible effects, which we shall now consider.

The first effect, as in the case of monatomic substances, is that $\ln M$ must be replaced by the suitably weighted sum

$$\Sigma_i \, x_i \ln M_i \qquad\qquad 4.\,65.\,1$$

where x_i is the mole fraction of the particular isotope i having a molar mass M_i. Similarly $\ln \Theta_r$ must be replaced by

$$\Sigma_i \, x_i \ln \Theta_{ri} \qquad\qquad 4.\,65.\,2$$

where Θ_{ri} is the value of Θ_r for the particular isotope i. The terms in Θ_v must similarly be replaced by suitably weighted averages. It should not be necessary to give details, especially since in almost all cases it is sufficiently accurate to replace these averaging rules by the simpler rules of replacing

$$M \text{ by } \Sigma_i \, x_i \, M_i \qquad\qquad 4.\,65.\,3$$

$$\Theta_r \text{ by } \Sigma_i \, x_i \, \Theta_{ri} \qquad\qquad 4.\,65.\,4$$

$$\Theta_v \text{ by } \Sigma_i \, x_i \, \Theta_{vi} \qquad\qquad 4.\,65.\,5$$

It is only in the cases of H_2, D_2 and possibly other very light molecules containing H, D that these simpler averaging rules may not always be sufficiently accurate.

The term H^0 occurring in H_m and in μ, but not in S_m, must likewise be replaced by the weighted average

$$\Sigma_i\, x_i\, H_i^0 \qquad\qquad 4.\,65.\,6$$

The second effect is that any phase whether solid, liquid or gaseous, consisting of a mixture of isotopic molecules in mole fractions x_i, has an entropy per mole exceeding the entropy per mole of similar phases of the pure isotopes at the same temperature and pressure, and this excess is

$$-R\,\Sigma_i\, x_i \ln x_i \qquad\qquad 4.\,65.\,7$$

which is always positive since $x_i < 1$. As long as the solid and gas have the same isotopic composition, the two terms of the form (7) cancel and so contribute nothing to $\Theta^{\frac{5}{2}} o$.

The third effect to be considered is that associated with difference in symmetry. Let us consider the particular example of Cl_2. There are three kinds of molecules $^{35}Cl\ ^{35}Cl$, $^{37}Cl\ ^{37}Cl$ and $^{35}Cl\ ^{37}Cl$. For the molecules $^{35}Cl\ ^{35}Cl$ and $^{37}Cl\ ^{37}Cl$ the symmetry number σ is 2, while for the molecule $^{35}Cl\ ^{37}Cl$ it is 1. In the crystal, on the other hand, o for $^{35}Cl\ ^{37}Cl$ will have the value 2 because each molecule can be reversed to give a physically distinct state of the crystal of effectively equal energy, whereas for $^{35}Cl\ ^{35}Cl$ and $^{37}Cl\ ^{37}Cl$ there are not two distinguishable orientations of effectively equal energy and so o is 1. Thus the product σo has the same value 2 for all three types of molecules. Ignoring the isotopic composition means then assigning to $^{35}Cl\ ^{37}Cl$ a fictitious value of $\sigma = 2$ instead of $\sigma = 1$ and to o a fictitious value $o = 1$ instead of $o = 2$. When we compare the entropy of the gas and the crystal, and it is only in such comparisons that the values assigned to S_m have any significance, the two errors cancel.

It is instructive to compare the relative behaviours of CO and N_2 with those of $^{35}Cl\ ^{37}Cl$ and $^{35}Cl\ ^{35}Cl$. We saw in § 4. 61 that for CO the value of o is 2 while of course $\sigma = 1$. We should however obtain correct results if we assumed as for N_2 that $o = 1$ with $\sigma = 2$, using this *effective symmetry number* because CO is an *effectively symmetrical molecule*.

The same principle holds in more complicated cases. For example comparing the isotopic molecules CH_4, CH_3D, CH_2D_2 we see that for the first $\sigma = 12$, $o = 1$, for the second $\sigma = 3$, $o = 4$ and for the third $\sigma = 2$, $o = 6$ so that in all three cases the product σo is 12.

§ 4. 66 THIRD PRINCIPLE OF THERMODYNAMICS AND NERNST'S HEAT THEOREM

We recall our formulation of the third principle in § 1. 63, which we now repeat.

By the standard methods of statistical thermodynamics it is possible to derive for certain entropy changes general formulae which cannot be derived from the zeroth, first or second principles of classical thermodynamics.

In the present chapter we have had three distinct examples of this type.

In the first place we have quoted a result of completely general validity for the entropy constant of gases at sufficiently high temperatures, namely the formula (4. 56. 3) or (4. 59. 2) for Θ†.

In the second place we have quoted a result of completely general validity for the increase of entropy when isotopes, or for that matter any other very similar molecules, are mixed at constant temperature and pressure.

In the third place we have quoted a result concerning the conventional zero-entropy of a crystal, namely that o is usually but not always unity.

This last result, in the form quoted, is not altogether satisfactory because it admits exceptions without indicating how or when these occur. It is therefore desirable to try to replace this statement by a more definite statement not admitting exceptions. The following statement fulfils these requirements.

If ΔS denotes the increase in entropy in any isothermal change which we represent symbolically by

$$a \to \beta \qquad\qquad 4.\,66.\,1$$

and we extrapolate ΔS to $T = 0$ smoothly in the usual way, then if the states a and β are both internally stable, or if any kind of internal metastability present is not affected by the change $a \to \beta$,

$$\underset{T \to 0}{\mathrm{Lt}}\, \Delta S = 0 \qquad\qquad 4.\,66.\,2$$

If on the other hand a is internally metastable, while β is stable, so that the change $a \to \beta$ removes the metastability, then

$$\underset{T \to 0}{\mathrm{Lt}}\, \Delta S < 0 \qquad\qquad 4.\,66.\,3$$

The case where a is stable and β metastable does not arise, since the

change $\alpha \to \beta$ would then be impossible. The above statements constitute an amended form * of a theorem first stated by Nernst and usually known as *Nernst's heat theorem*.

We shall now verify that the behaviour already described of crystals in the limit $T \to 0$ is in accord with the above general statement.

We observe that the several exceptional crystals for which o is not unity are in fact in internally metastable states with some form of randomness of arrangement of the molecules. If by any means it were possible to change such a crystal to the stable completely ordered modifications o would be reduced from a value greater than unity to the value unity and so (3) is satisfied.

Examples of changes satisfying (2) are allotropic changes such as

$$\text{white tin} \to \text{grey tin}$$

$$\text{monoclinic sulphur} \to \text{rhombic sulphur}$$

In each of these examples, although at low temperatures and ordinary pressures the first form is metastable with respect to the second, both forms are completely stable with respect to internal changes. In each case for both phases $o = 1$ and so the equality (2) is obeyed.

Another interesting example is that of helium, the only substance which remains liquid down to $T = 0$. The liquid is changed to solid under pressure. The relation between the pressure and freezing temperature is shown in fig. 4. 12, from which it is clear that

$$\underset{T \to 0}{\text{Lt}} \frac{dP}{dT} = 0 \qquad \qquad 4.\,66.\,4$$

But according to the Clapeyron relation (4. 41. 10) this is equivalent to

$$\underset{T \to 0}{\text{Lt}} \frac{\Delta S}{\Delta V} = 0 \qquad \qquad 4.\,66.\,5$$

But ΔV is certainly finite and so (5) implies

$$\underset{T \to 0}{\text{Lt}} \Delta S = 0 \qquad \qquad 4.\,66.\,6$$

The most numerous and important examples of the relation (2) are those of chemical reactions between solid phases, for example

$$\text{Ag} + \text{I} \to \text{AgI}$$
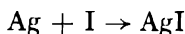
These will be discussed in § 7. 14.

* See Simon, *Ergebn. exakt. Naturw* 1930 **9** 222.

§ 4. 67 THERMAL EXPANSION AT LOW TEMPERATURES

It is an experimental fact that the coefficient of thermal expansion of solids and of liquid helium tends towards zero as the temperature
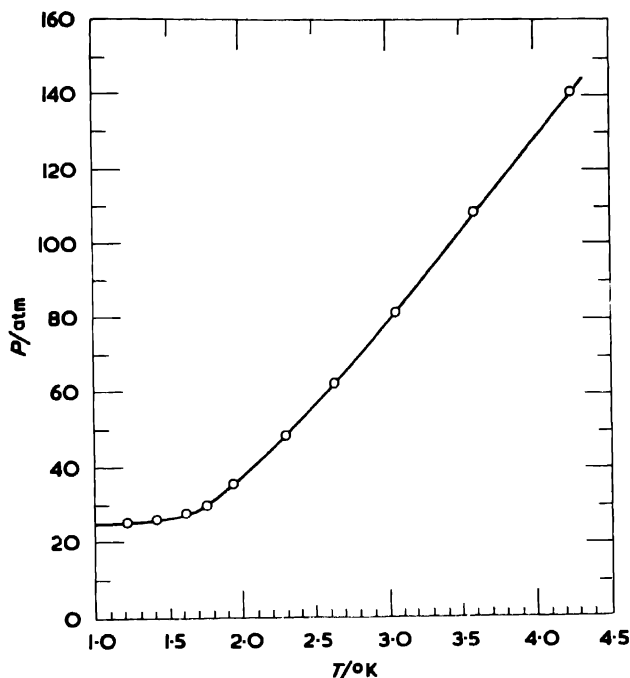
Fig 4 12. Melting curve of helium

is decreased. But according to Maxwell's relation (3. 04. 4), this implies that

$$\operatorname*{Lt}_{T \to 0} \left(\frac{\partial S}{\partial P}\right)_T = 0 \qquad\qquad 4.\ 67.\ 1$$

If we integrate this from P^I to P^{II}, we obtain

$$\operatorname*{Lt}_{T \to 0} \{S\,(T,\,P^{II}) - S\,(T,\,P^I)\,\} = 0 \qquad\qquad 4.\ 67.\ 2$$

which is in accordance with the general relation (4. 66. 2).

This is the only example of the application of (4. 66. 2) to a simple physical change which we can discuss at this stage. In chapter 12 we shall consider an interesting application to variation of the strength of an applied magnetic field.

§ 4. 68 UNATTAINABILITY OF ABSOLUTE ZERO

The general laws formulated in the preceding sections concerning the behaviour of matter extrapolated to $T = 0$ are equivalent to the following principle *:

➤*It is impossible by any procedure, no matter how idealized, to reduce the temperature of any system to the absolute zero in a finite number of operations.*

We shall now prove this equivalence. Let us consider a process (e.g. change of volume, change of external field, allotropic change) denoted formally by

$$a \to \beta \qquad\qquad 4.68.1$$

We shall use the superscripts a and β to denote properties of the system in the states a and β respectively. Then the molar entropies of the system in these two states depend on the temperature according to the formulae

$$S_m^a = S_m^{0a} + \int_0^T \frac{C^a}{T} \, \mathrm{d}T \qquad\qquad 4.68.2$$

$$S_m^\beta = S_m^{0\beta} + \int_0^T \frac{C^\beta}{T} \, \mathrm{d}T \qquad\qquad 4.68.3$$

where S_m^{0a}, $S_m^{0\beta}$ are the limiting values of S_m^a, S_m^β for $T \to 0$. It is known from quantum theory that both the integrals converge. Suppose now that we start with the system in the state a at the temperature T' and that we can make the process $a \to \beta$ take place adiabatically. Let the final temperature after the system has reached the state β be T''. We shall now consider the possibility or impossibility of T'' being zero. From the second principle of thermodynamics we know that for an adiabatic process defined by its initial and final states the entropy increases if there is any irreversible change and remains constant if the change is completely reversible. It is therefore clear that the chances of attaining as low a final T as possible are most favourable when the change is completely reversible. We need therefore consider only such changes. For a reversible adiabatic change (1) we have then by (2) and (3)

$$S_m^{0a} + \int_0^{T'} \frac{C^a}{T} \, \mathrm{d}T = S_m^{0\beta} + \int_0^{T''} \frac{C^\beta}{T} \, \mathrm{d}T \qquad\qquad 4.68.4$$

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* See Simon, *Science Museum Handbook* 1937 **3** p. 61. All earlier discussions are unnecessarily restricted.

Cf. Fowler and Guggenheim, *Statistical Thermodynamics* 1939 § 538.

If T'' is to be zero, we must then have

$$S_m^{0\beta} - S_m^{0\alpha} = \int_0^{T'} \frac{C^\alpha}{T} \, dT \qquad \text{4. 68. 5}$$

Now if $S_m^{0\beta} - S_m^{0\alpha} > 0$ it will always be possible to choose an initial T' satisfying (5) and by making the process $\alpha \to \beta$ take place from this initial T' it will be possible to reach $T'' = 0$. From the premise of the unattainability of $T = 0$ we can therefore conclude that

$$S_m^{0\beta} < S_m^{0\alpha} \qquad \text{4. 68. 6}$$

Similarly we can show that if we can make the reverse process take place reversibly and adiabatically then we could reach $T'' = 0$ from an initial temperature T' satisfying

$$S_m^{0\alpha} - S_m^{0\beta} = \int_0^{T'} \frac{C^\beta}{T} \, dT \qquad \text{4. 68. 7}$$

Further if $S_m^{0\alpha} - S_m^{0\beta} > 0$, we can always choose an initial T' satisfying (7). From the unattainability of $T = 0$ we can therefore conclude that

$$S_m^{0\alpha} < S_m^{0\beta} \qquad \text{4. 68. 8}$$

From (6) and (8) we deduce

$$S_m^{0\alpha} = S_m^{0\beta} \qquad \text{4. 68. 9}$$

which is precisely formula (4. 66. 2) of Nernst's heat theorem.

We can also show conversely that given (9), neither the process $\alpha \to \beta$ nor the reverse process $\beta \to \alpha$ can be used to reach $T = 0$. For, assuming (9) to be true, we now have for the adiabatic process $\alpha \to \beta$ the initial temperature T' and the final temperature T'' related by

$$\int_0^{T'} \frac{C^\alpha}{T} \, dT = \int_0^{T''} \frac{C^\beta}{T} \, dT \qquad \text{4. 68. 10}$$

To reach $T'' = 0$ we should require

$$\int_0^{T'} \frac{C^\alpha}{T} \, dT = 0 \qquad \text{4. 68. 11}$$

But, since $C^\alpha > 0$ always, for any non-zero T', it is impossible to satisfy (11). Hence the process $\alpha \to \beta$ can not be used to reach $T = 0$. The proof for the reverse process $\beta \to \alpha$ is exactly similar.

In the above argument we have assumed that the states α and β are

connected by reversible paths. If all the phases concerned are phases in complete internal equilibrium the changes concerned must presumably be regarded as reversible. If any phase occurs naturally in metastable internal equilibrium, a process affecting it may or may not disturb the frozen metastability. If it does not disturb it, then the change may still be regarded as reversible, but otherwise it will be a natural irreversible change. We shall now verify that by using internally metastable phases we are still unable to reach $T = 0$. In fact as foreshadowed above the irreversibility involved makes the task more difficult.

Suppose for example that α is internally metastable, while β is internally stable. Then according to (4. 66. 3) of Nernst's heat theorem

$$S_m^{0\alpha} > S_m^{0\beta} \qquad\qquad 4.\ 68.\ 12$$

But the change $\alpha \to \beta$ is a natural irreversible process and the opposite change is impossible; hence the adiabatic change $\alpha \to \beta$ takes place with increase of entropy, so that

$$S_m^{0\alpha} + \int_0^{T'} \frac{C^\alpha}{T}\, \mathrm{d}T < S_m^{0\beta} + \int_0^{T'} \frac{C^\beta}{T}\, \mathrm{d}T \qquad\qquad 4.\ 68.\ 13$$

Thus to attain $T'' = 0$, we must have

$$\int_0^{T'} \frac{C^\alpha}{T}\, \mathrm{d}T < S_m^{0\beta} - S_m^{0\alpha} < 0 \qquad\qquad 4.\ 68.\ 14$$

using (12). But since $C^\alpha > 0$ always, it is impossible to satisfy (14) and so we again find it impossible to reach $T = 0$.

We shall revert to the subject of the unattainability of $T = 0$ at the end of chapter 12 on magnetic systems.

§ 4. 69 INTERFACIAL LAYERS

We complete this chapter by a consideration of interfacial layers. In a one component system we cannot usually have more than one liquid phase and so we need consider only the interface between a liquid and its vapour. The interfacial tension of such an interface is usually called the *surface tension of the liquid*.

As we have seen in § 4. 40 a one component system with two bulk phases has one degree of freedom. We may accordingly treat the temperature as the independent variable; the pressure is then determined by the temperature. Thus the properties of the interfacial layer, in particular the surface tension, will be completely determined

by the temperature. Our main task is therefore to consider how the surface tension depends on the temperature.

§ 4. 70 TEMPERATURE DEPENDENCE OF SURFACE TENSION

We begin with formula (1. 55. 3)

$$- \mathrm{d}\gamma = S^\sigma \, \mathrm{d}T - \tau \mathrm{d}P + \Gamma \mathrm{d}\mu \qquad \qquad 4.\,70.\,1$$

where we have dropped the subscript $_u$ in S^σ, which we henceforth assume to refer to unit area.

From the equilibrium between the liquid phase, denoted by the superscript ^{L}, and the gas phase, denoted by the superscript ^{G}, we have as in § 4. 41

$$\mathrm{d}\mu = - S_m^L \, \mathrm{d}T + V_m^L \, \mathrm{d}P = - S_m^G \, \mathrm{d}T + V_m^G \, \mathrm{d}P \qquad 4.\,70.\,2$$

When we eliminate $\mathrm{d}\mu$ and $\mathrm{d}P$ from (1) and (2) we obtain

$$- \frac{\mathrm{d}\gamma}{\mathrm{d}T} = (S^\sigma - \Gamma S_m^L) - (\tau - \Gamma V_m^L) \frac{S_m^G - S_m^L}{V_m^G - V_m^L} \qquad 4.\,70.\,3$$

This formula relates the temperature coefficient of the surface tension to certain entropy changes. Before we examine this formula in any detail, we shall show how it can be transformed to another relation involving energy changes instead of entropy changes.

For the two bulk phases we have as usual

$$\mu = G_m^L = U_m^L - TS_m^L + PV_m^L \qquad \qquad 4.\,70.\,4$$

$$\mu = G_m^G = U_m^G - TS_m^G + PV_m^G \qquad \qquad 4.\,70.\,5$$

For the surface layer we have by applying to unit area the formulae of § 1. 54

$$\Gamma \mu = G^\sigma = U^\sigma - TS^\sigma + P\tau - \gamma \qquad \qquad 4.\,70.\,6$$

We now use (4), (5) and (6) to eliminate S_m^L, S_m^G and S^σ from (3). We obtain

$$- T \frac{\mathrm{d}\gamma}{\mathrm{d}T} = (U^\sigma - \Gamma U_m^L) + P(\tau - \Gamma V_m^L) - \gamma$$

$$- (\tau - \Gamma V_m^L) \frac{U_m^G - U_m^L}{V_m^G - V_m^L} - P (\tau - \Gamma V_m^L) \qquad 4.\,70.\,7$$

The terms containing P cancel and (7) reduces to

$$\gamma - T\frac{d\gamma}{dT} = (U^\sigma - \Gamma U_m^L) - (\tau - \Gamma V_m^L) \frac{U_m^G - U_m^L}{V_m^G - V_m^L} \qquad 4.\,70.\,8$$

§ 4. 71 INVARIANCE OF RELATIONS

We recall that according to the definition in § 1. 51 of a surface phase the properties associated with it depend on the position of the boundaries AA' and BB' in fig. 1. 2. We shall henceforth refer to these as the Lσ and the Gσ boundaries respectively. Since the precise placing of these boundaries is arbitrary, the values assigned to such quantities as τ, Γ, S^σ, U^σ are also arbitrary. We can nevertheless verify that our formulae are invariant with respect to shifts of either or both of the boundaries. It is hardly necessary to mention that the intensive variables T, P and μ are unaffected by shifts of either boundary. It is also clear from the definition of γ in § 1. 52 that its value is invariant.

Let us now consider a shift of the plane boundary Lσ through a distance $\delta\tau$ away from the gas phase. Then Γ becomes increased by the number of moles in a cylinder of liquid of height $\delta\tau$, of cross-section unity and consequently of volume $\delta\tau$. Thus Γ becomes increased by $\delta\tau/V_m^L$. It follows immediately that $\tau - \Gamma V_m^L$ remains invariant. Similarly S^σ becomes increased by the entropy in a cylinder of liquid of volume $\delta\tau$, that is to say by an amount $S_m^L \delta\tau/V_m^L$. It follows immediately that $S^\sigma - \Gamma S_m^L$ remains invariant. Precisely similar considerations show that $U^\sigma - \Gamma U_m^L$ remains invariant.

We have now to consider a similar shift of the Gσ boundary through a distance $\delta\tau$ away from the liquid phase. Then Γ is increased by $\delta\tau/V_m^G$, and so $(\tau - \Gamma V_m^L)$ is increased by $(V_m^G - V_m^L) \delta\tau/V_m^G$. Similarly $(S^\sigma - S_m^L)$ is increased by $(S_m^G - S_m^L) \delta\tau/V_m^G$. When we insert these values into (4. 70. 3) we see that the resulting variation vanishes. The same holds for (4. 70. 8).

§ 4. 72 SIMPLIFYING APPROXIMATION

The formulae of § 4. 70 are strictly accurate and involve no assumptions or approximations concerning the structure of the interfacial layer. We shall see that they can be greatly simplified by making use of our knowledge concerning this layer.

In § 4. 34 we mentioned that, at temperatures well below the critical, PV_m^L is small compared with RT and may usually be ignored. In the

interfacial layer the density is comparable to that in the liquid phase so that τ/Γ is comparable to V_m^{L} and negligible compared with V_m^{G}. Consequently the terms containing the factor $(\tau - \Gamma V_m^{\mathrm{L}})/(V_m^{\mathrm{G}} - V_m^{\mathrm{L}})$ may be neglected. Formulae (4. 70. 3) and (4. 70. 8) then reduce to

$$-\frac{d\gamma}{dT} = S^{\sigma} - \Gamma S_m^{\mathrm{L}} \qquad \text{4. 72. 1}$$

$$\gamma - T\frac{d\gamma}{dT} = U^{\sigma} - \Gamma U_m^{\mathrm{L}} \qquad \text{4. 72. 2}$$

respectively.

It is worth noticing that the right side of (1) is the entropy of unit area of surface less the entropy of the same material content of liquid and the right side of (2) is the energy of unit area of surface less the energy of the same material content of liquid. More pictorially we may say that when unit area of surface is created isothermally and reversibly, the work done on the system is γ, the heat absorbed by the system is the right side of (1) multiplied by T, and the increase of energy, the sum of these two quantities, is equal to the right side of (2).

If however we are making the above simplifying approximations, then by making them at an earlier stage we can considerably simplify the derivations. We accordingly replace (4. 70. 1) by the approximation

$$-d\gamma = S^{\sigma} dT + \Gamma d\mu \qquad \text{4. 72. 3}$$

and (4. 70. 2) by the approximation

$$d\mu = -S_m^{\mathrm{L}} dT = -S_m^{\mathrm{G}} dT + RT d\ln P \qquad \text{4. 72. 4}$$

Eliminating $d\mu$ from (3) and (4) we obtain immediately

$$-d\gamma = (S^{\sigma} - \Gamma S_m^{\mathrm{L}}) dT \qquad \text{4. 72. 5}$$

in agreement with (1).

Furthermore we replace (4. 70. 4) by the approximation

$$\mu = U_m^{\mathrm{L}} - TS_m^{\mathrm{L}} \qquad \text{4. 72. 6}$$

and (4. 70. 6) by the approximation

$$\Gamma\mu = U^{\sigma} - TS^{\sigma} - \gamma \qquad \text{4. 72. 7}$$

Eliminating S^{σ} and S_m^{L} from (5), (6) and (7) we recover (2).

We conclude this discussion with a warning against indiscriminately

using the simplified formulae of this section in the neighbourhood of the critical point. The necessary condition for their use is that

$$\tau/\Gamma - V_m^L \ll V_m^G - V_m^L \qquad 4.\,72.\,8$$

In the neighbourhood of the critical temperature V_m^L becomes nearly as great as V_m^G and this condition may no longer be taken for granted.

§ 4. 73 VAPOUR PRESSURE OF SMALL DROPS

Fig. 4. 13 represents a small spherical drop and a portion of liquid in bulk both at the same temperature. We denote the interiors of these
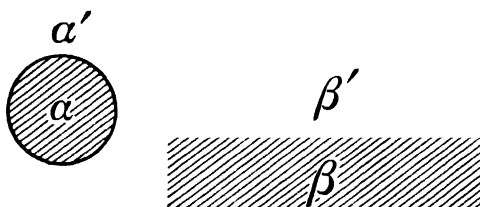
Fig 4. 13. Vapour pressure of droplet.

liquid phases by α, β respectively and the vapour immediately outside them by α', β' respectively. Let us assume that the external pressures $P^{\alpha'}$ and $P^{\beta'}$ are equal, that is

$$P^{\alpha'} = P^{\beta'} \qquad 4.\,73.\,1$$

Then, according to (1. 56. 10) the pressure P^α at the interior α of the drop is greater than that P^β of the liquid in bulk by

$$P^\alpha - P^\beta = \frac{2}{r}\gamma \qquad 4.\,73.\,2$$

where r is the radius of the drop. But according to (4. 50. 11) the fugacity $p^\star$ is related to the pressure P by

$$\frac{\mathrm{d} \ln p^\star}{\mathrm{d}P} = \frac{V_m^L}{RT} \qquad 4.\,73.\,3$$

If then we neglect the compressibility of the liquid, the fugacity $p^{\star\alpha}$ of the liquid in the drop is related to the fugacity $p^{\star\beta}$ of the liquid in bulk by

$$RT \ln \frac{p^{\star\alpha}}{p^{\star\beta}} = (P^\alpha - P^\beta)\, V_m^L \qquad 4.\,73.\,4$$

Comparing (2) and (4) we find

$$RT \ln \frac{p^{*\alpha}}{p^{*\beta}} = \frac{2}{r} \gamma V_m^L \qquad 4.\,73.\,5$$

If we neglect deviations of the vapour from a perfect gas, we may replace fugacities p^* by vapour pressures p and so obtain

$$RT \ln \frac{p^\alpha}{p^\beta} = \frac{2}{r} \gamma V_m^L \qquad 4.\,73.\,6$$

We see then that at the same external pressure the small drop always has a greater fugacity and vapour pressure than the bulk liquid. Vapour will distil from the drop to the liquid and as the drop becomes smaller its vapour pressure increases still more. Thus small drops are essentially metastable relatively to the liquid in bulk.

§ 4. 74 EMPIRICAL TEMPERATURE DEPENDENCE OF SURFACE TENSION

Since the surface tension of a liquid decreases with increasing temperature and vanishes at the critical point, the simplest possible form of empirical relation between γ and T is

$$\gamma = \gamma_0 \left(1 - \frac{T}{T_c} \right)^{1+r} \qquad 4.\,74.\,1$$

where γ_0 and r are constants. For the substances having the simplest and most symmetrical molecules such as Ne, A, N_2, O_2 excellent agreement with the experimental data is obtained with $r = 2/9$ as is shown in table 4. 11. The data at the foot of this table will be discussed in § 4. 75.

The reason for the particular choice $r = 2/9$ will be explained shortly. Ferguson * in a review of the experimental data for ten esters and four other organic compounds found $r = 0.210 \pm 0.015$, which does not differ significantly from the value 2/9 adopted above. Van der Waals at a much earlier date suggested the value $r = 0.234$, but the experimental data do not support this value.

Another type of formula relates the surface tension γ to the coexisting molar volumes V^L of the liquid and V^G of the vapour. The simplest satisfactory formula of this type is the following ·

$$\gamma \gamma^{-\frac{2}{3}} \propto (1 - T/T_c) \qquad 4.\,74.\,2$$

* Ferguson, *Trans. Faraday Soc.* 1923 **19** 407; *Proc. Phys. Soc. Lond.* 1940 **52** 759.

where y is defined by

$$y = \frac{1}{V_m^L} - \frac{1}{V_m^G} \qquad \text{4. 74. 3}$$

or

$$y V_c = \frac{\varrho^L - \varrho^G}{\varrho_c} \qquad \text{4. 74. 4}$$

This formula, due to Katayama [*], is a striking improvement over the older and less accurate formula of Eötvos, which contained V^L instead of y^{-1}. This was shown by Katayama for various organic compounds and we shall now verify that this is also the case for the substances having the simplest molecules.

TABLE 4 11

$$\gamma = \gamma_0 \, (1 - T/T_c)^{11/9}$$

Ne			A			N$_2$			O$_2$		
$T_c = 44.8\,°\text{K}$			$T_c = 150.7\,°\text{K}$			$T_c = 126.0\,°\text{K}$			$T_c = 154.3\,°\text{K}$		
$\gamma_0 = 15.1$ dyne cm^{-1}			$\gamma_0 = 36.31$ dyne cm^{-1}			$\gamma_0 = 28.4$ dyne cm^{-1}			$\gamma_0 = 38.4$ dyne cm^{-1}		
T	γ/dyne cm^{-1}		T	γ/dyne cm^{-1}		T	γ/dyne cm^{-1}		T	γ/dyne cm^{-1}	
°K	calc.	obs.	°K	calc.	obs.	°K	calc.	obs.	°K	calc.	obs.
24.8	5.64	5.61	85.0	13.16	13.19	70.0	10.54	10.53	70.0	18.34	18.35
25.7	5.33	5.33	87.0	12.67	12.68	75.0	9.40	9.39	75.0	17.02	17.0
26.6	5.02	4.99	90.0	11 95	11.91	80.0	8.29	8.27	80.0	15.72	15.73
27.4	4.75	4.69				85.0	7.20	7.20	85.0	14.44	14.5
28.3	4.45	4.44				90.0	6.14	6.16	90.0	13.17	13.23
$V_c = 41.7$ cm^3 mole^{-1}			$V_c = 75.3$ cm^3 mole^{-1}			$V_c = 90.2$ cm^3 mole^{-1}			$V_c = 74.5$ cm^3 mole^{-1}		
$\gamma_0 V_0^{2/3} T_c^{-1} =$			$\gamma_0 V_c^{2/3} T_c^{-1} =$			$\gamma_0 V_c^{2/3} T_c^{-1} =$			$\gamma_0 V_c^{2/3} T_c^{-1} =$		
4.05 erg deg^{-1} mole$^{-\frac{2}{3}}$			4.3 erg deg^{-1} mole$^{-\frac{2}{3}}$			4.5 erg deg^{-1} mole$^{-\frac{2}{3}}$			4.4 erg deg^{-1} mole$^{-\frac{2}{3}}$		

In § 4. 53 we verified that the substances having the simplest molecules follow with a high degree of accuracy formula (4. 53. 9), namely

$$\frac{\varrho^L - \varrho^G}{\varrho_c} = \frac{7}{2} \left(1 - \frac{T}{T_c} \right)^{\frac{1}{3}} \qquad \text{4. 74. 5}$$

Using the definition (4) of y, this can be written

$$y \propto \left(1 - \frac{T}{T_c} \right)^{\frac{1}{3}} \qquad \text{4. 74. 6}$$

[*] Katayama, *Sci. Rep. Tôhoku Univ.* 1916 **4** 373.

If we now eliminate y between (2) and (6), we obtain

$$\gamma \propto \left(1 - \frac{T}{T_c}\right)^{1\frac{2}{9}} \qquad\qquad 4.\,74.\,7$$

of the form (1) with $r = 2/9$. It follows that the verification of (7) in table 4. 11 and the verification of (5) in fig. 4. 10 together constitute a verification of (2).

If instead of eliminating y between (2) and (6), we eliminate T/T_c between the same formulae we obtain

$$\gamma \propto y^{3\frac{2}{9}} \qquad\qquad 4.\,74.\,8$$

The better known relation of Macleod * with an index 4 instead of $3\frac{2}{9}$ is less accurate, at least for the substances having the simplest molecules. Actually for the half dozen organic compounds considered by Macleod it is clear that γ in fact varies as some power of y less than 4.

§ 4. 75 CORRESPONDING STATES APPLIED TO SURFACE TENSIONS

The principle of corresponding states, so far as it is applicable at all to surfaces, can on physical grounds be expected to hold only for substances having the simplest and most symmetrical molecules.

According to the principle it is clear from dimensional considerations that $\gamma V_c^{2/3} T_c^{-1}$ should be a common function of T/T_c for substances obeying the principle. In particular, if these substances obey (4. 74. 1), then $\gamma_0 V_c^{2/3} T_c^{-1}$ should have a common value. The data † at the bottom of table 4. 11 show that this is in fact the case within about $\pm\ 2\ \%$ for A, N_2, O_2 while the value for Ne deviates by rather less than 10 %.

§ 4. 76 SORPTION OF A SINGLE GAS

In our discussion of the interface between a liquid and a gas the surface area A was first introduced as an independent variable. The interfacial tension γ was then introduced through the relation

$$w = \gamma \mathrm{d}A \qquad\qquad 4.\,76.\,1\text{`}$$

Both A and γ are well defined measurable quantities. The situation for a solid-gas interface is altogether different. The area of the interface

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* Macleod, *Trans. Faraday Soc.* 1923 **19** 38.

† For details see Guggenheim, *J. Chem. Phys.* 1945 **13** 259.

may be difficult, if not impossible, to measure accurately especially if the solid is porous or a powder. Furthermore the surface area can not be varied reversibly and consequently there is no relation such as (1). There is no quantity analogous to interfacial tension. For discussing the equilibrium between a gas and a solid-gas interface a completely different approach is called for.

The name *sorption* was coined by McBain [*] to include as special cases *absorption* and *adsorption* which should be restricted to proven cases of solution and surface condensation respectively.

In the following discussion of sorption we shall assume that the sorbed gas is a single substance, but no restriction will be placed on the nature of the sorbent except that we assume absence of hysteresis. In other words we shall consider the equilibrium between a single gas and a sorbent which may be a piece of platinum gauze, a lump of impure charcoal or some powdered glass or in fact almost anything.

The first question to be considered is how to measure sorption. This is done by a *sorption balance*. Essentially the sorbent is suspended on a spring balance so that its weight, and thence its mass, can be compared in vacuo and in equilibrium with a surrounding gas at a given temperature and pressure. If no correction is applied for the buoyancy due to the surrounding gas, the apparent increase in mass recorded by the balance is equal to that of the excess quantity of the sorbed substance due to sorption over and above the quantity which would be contained in the same volume, at the same temperature and pressure, in the absence of the sorbent. This mass divided by the molar mass of the gas is equal to the excess number of moles of the sorbed substance due to sorption over and above the number of moles of the gas which would be contained in the same volume, at the same temperature and pressure, in the absence of the sorbent. We denote this number of moles by n^a and we shall call n^a the *sorbed excess number of moles*. This quantity is the simplest and most convenient measure of sorption. At a first approach it might seem that a simpler quantity would be the number of moles of sorbed substance contained by the sorbent. Such a quantity would have to be calculated by adding to n^a the quantity $\varrho V^s / M$ where ϱ is the density of the gas, M is the molar mass of the gas and V^s is the volume of the sorbent. On reflection it becomes clear that V^s is a rather vague quantity, difficult if not impossible to measure accurately especially if the sorbent is porous or a powder. This difficulty is completely avoided by using n^a, without any buoyancy correction

[*] McBain, *Phil. Mag.* 1909 **18** 916.

as our measure of sorption. We shall adopt this approach and shall consider how n^a is related to the temperature and pressure.

§ 4. 77 TEMPERATURE DEPENDENCE OF SORPTION

We consider a vessel of volume V containing the sorbent and n moles of the sorbate at the temperature T and pressure P. If V_m denotes the molar volume of gaseous sorbate, then according to the definition of n^a in the previous section we have

$$V = (n - n^a) V_m \qquad 4.77.1$$

We now combine Maxwell's relation (3. 04. 4) with (1) and obtain

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P = (n - n^a)\left(\frac{\partial V_m}{\partial T}\right)_P - \left(\frac{\partial n^a}{\partial T}\right)_P V_m \qquad 4.77.2$$

and consequently

$$-\left(\frac{\partial S}{\partial n^a}\right)_T = -\left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial n^a}\right)_T$$

$$= (n - n^a)\left(\frac{\partial V_m}{\partial T}\right)_P \left(\frac{\partial P}{\partial n^a}\right)_T - \left(\frac{\partial n^a}{\partial T}\right)_P V_m \left(\frac{\partial P}{\partial n^a}\right)_T$$

$$= (n - n^a)\left(\frac{\partial V_m}{\partial T}\right)_P \left(\frac{\partial P}{\partial n^a}\right)_T + \left(\frac{\partial P}{\partial T}\right)_{n^a} V_m \qquad 4.77.3$$

We now compare our system with another system consisting of a vessel of the same volume V containing the same gas at the same temperature and pressure but without any sorbent. We shall use dashed symbols for quantities relating to this second system when they may differ from those relating to the first system. We have then

$$n' = n - n^a \qquad 4.77.4$$

Moreover since both systems are in equilibrium and the gas is in identical conditions we have also

$$\mu' = \mu \qquad 4.77.5$$

If now we denote by ΔS_m the entropy increase in the first system per unit decrease of n^a brought about by decreasing the pressure, we have according to (3)

$$\Delta S_m = (n - n^a)\left(\frac{\partial V_m}{\partial T}\right)_P \left(\frac{\partial P}{\partial n^a}\right)_T + \left(\frac{\partial P}{\partial T}\right)_{n^a} V_m \qquad 4.77.6$$

If further we denote by $\Delta'S$ the entropy increase in the second system corresponding to the same decrease in pressure, we have

$$\Delta'S_m = n' \left(\frac{\partial V_m}{\partial T}\right)_P \left(\frac{\partial P}{\partial n^a}\right)_T \qquad \text{4. 77. 7}$$

Subtracting (7) from (6) and using (4) we obtain

$$\Delta S_m - \Delta'S_m = \left(\frac{\partial P}{\partial T}\right)_{n^a} V_m \qquad \text{4. 77. 8}$$

or

$$T\Delta S_m - T\Delta'S_m = T\left(\frac{\partial P}{\partial T}\right)_{n^a} V_m \qquad \text{4. 77. 9}$$

It follows immediately from (5) that

$$\Delta\mu = \Delta'\mu \qquad \text{4. 77. 10}$$

and so subtracting (10) from (9) we obtain the alternative formula

$$\Delta H_m - \Delta'H_m = T\left(\frac{\partial P}{\partial T}\right)_{n^a} V_m \qquad \text{4. 77. 11}$$

The left side of either (9) or (11) may be called the *molar equilibrium heat of desorption* [*]. It is the heat that must be supplied per unit decrease of n^a resulting from decrease of pressure under isothermal equilibrium conditions less the heat that must be supplied to the second system when the pressure is isothermally decreased by the same amount. We emphasize that every quantity occurring in (9) and (11) is experimentally determinable without the use of any approximation or extraneous assumption. This contrasts with some other formulae which contain quantities such as the surface area of the sorbent, the spreading pressure, and the volume occupied by a sorbed molecule. Such quantities play their natural part as parameters in a kinetic or statistical mechanical theory of sorption, but, not being accurately measurable, they have no part in a treatment by classical thermodynamics.

In all normal applications the pressure will be sufficiently small to justify neglect of all virial coefficients higher than the second. We then have in accordance with (4. 14. 6)

$$V_m = \frac{RT}{P} + B \qquad \text{4. 77. 12}$$

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[*] The derivation of these formulae was presented to the Boston University Conference on Nucleation 1951, the proceedings of which are "still printing".

Substituting (12) into (9) and (11) we obtain

$$T\Delta S_m - T\Delta' S_m = \Delta H_m - \Delta' H_m$$

$$= RT^2 \left(\frac{\partial \ln P}{\partial T}\right)_{n^a} \left(1 + \frac{PB}{RT}\right) \qquad \text{4. 77. 13}$$

When the term in B is negligible, so that the gas is effectively perfect (13) reduces to a form derivable by more elementary methods.

CHAPTER 5

GASEOUS, LIQUID AND SOLID MIXTURES

§ 5. 01 INTRODUCTION

In this chapter we shall discuss homogeneous mixtures of two or more substances which do not react chemically. Consideration of chemical reactions is postponed to chapter 7. The mixtures may be gaseous, liquid or solid. So far as possible each of the several component substances of a mixture will be treated on the same basis. The opposite point of view is taken in chapter 6 where one substance is regarded as the solvent and the remaining substances as solutes.

As soon as we turn from single substances to mixtures we introduce the possibility of new degrees of freedom associated with differences of composition. For example we can have two or more liquid phases of different composition in mutual equilibrium.

There are no differences of principle between the treatments of systems of two components on the one hand and of systems of more than two components on the other. Many of the formulae for the former are however more compact than the corresponding formulae for the latter. For this reason we shall in some sections confine ourselves mainly if not entirely, to systems of two substances, i.e. *binary* systems.

§ 5. 02 MASS FRACTIONS AND MOLE FRACTIONS

In a mixture containing n_1, n_2,... units of the species 1, 2,... respectively the relative composition is conveniently described by the fractions

$$\frac{n_1}{\Sigma_i n_i}, \quad \frac{n_2}{\Sigma_i n_i}, \ldots$$

When the unit of each species is measured by its mass, these fractions are called *mass fractions* and are denoted by w_1, w_2,... It is usually more convenient to take as the unit of each species the mole. These fractions are then called *mole fractions* and are denoted by x_1, x_2,...

In a mixture of c components the c mass fractions are not independent since they are interrelated by

$$w_1 + w_2 + \ldots + w_c = 1 \qquad\qquad 5. 02. 1$$

Similarly the c mole fractions are interrelated by

$$x_1 + x_2 + \ldots + x_c = 1 \qquad 5.\,02.\,2$$

It will usually be convenient to choose $x_2, x_3, \ldots x_c$ as independent variables and x_1 as a dependent variable defined by

$$x_1 = 1 - x_2 - x_3 - \ldots - x_c \qquad 5.\,02.\,3$$

In the simple case of only two variables the subscript $_2$ may safely be dropped and we write x for x_2 and $1 - x$ for x_1.

§ 5. 03 NOTATION FOR CHANGES OF COMPOSITION

For a mixture of c components we shall usually choose as independent variables T, P, x_2, x_3, ... x_c. The most general variation of a function φ of these variables is then

$$d\varphi = \frac{\partial\varphi}{\partial T}\,dT + \frac{\partial\varphi}{\partial P}\,dP + \frac{\partial\varphi}{\partial x_2}\,dx_2 + \frac{\partial\varphi}{\partial x_3}\,dx_3 + \ldots + \frac{\partial\varphi}{\partial x_c}\,dx_c \qquad 5.\,03.\,1$$

It is convenient to introduce the abbreviation $D\varphi$ for the quantity defined by

$$D\varphi = \frac{\partial\varphi}{\partial x_2}\,dx_2 + \frac{\partial\varphi}{\partial x_3}\,dx_3 + \ldots + \frac{\partial\varphi}{\partial x_c}\,dx_c \qquad 5.\,03.\,2$$

By use of this notation formula (5. 03. 1) can be written in the shorter form

$$d\varphi = \frac{\partial\varphi}{\partial T}\,dT + \frac{\partial\varphi}{\partial P}\,dP + D\varphi \qquad 5.\,03.\,3$$

In the simple case of a binary mixture

$$D\varphi = \frac{\partial\varphi}{\partial x}\,dx \qquad 5.\,03.\,4$$

and the abbreviation is superfluous.

§ 5. 04 SPECIFIC AND MEAN MOLAR QUANTITIES

In a mixture consisting of n_1, n_2, ... n_c units of the species 1, 2, ... c respectively there is corresponding to each extensive property such as V an intensive property $V/(n_1 + n_2 + \ldots + n_c)$. When the unit of each species is measured by its mass, this quantity is called the *specific volume*. It is usually more convenient to take as the unit of each species

the mole. The above intensive quantity is then called the *mean molar volume* and it will be denoted by V_m. Thus, when each n denotes number of moles

$$V_m = V/(n_1 + n_2 + \ldots + n_c) \qquad 5.\ 04.\ 1$$

The definitions of other mean molar quantities are precisely analogous. For example we have

$$U_m = U/(n_1 + n_2 + \ldots + n_c) \qquad 5.\ 04.\ 2$$

$$S_m = S/(n_1 + n_2 + \ldots + n_c) \qquad 5.\ 04,\ 3$$

$$H_m = H/(n_1 + n_2 + \ldots + n_c) \qquad 5.\ 04,\ 4$$

$$G_m = G/(n_1 + n_2 + \ldots + n_c) \qquad 5.\ 04.\ 5$$

Since each mean molar quantity is obtained from the corresponding extensive quantity by division by the same divisor $n_1 + n_2 + \ldots + n_c$, it follows that for every relation between extensive properties there is an analogous relation between the mean molar quantities. For example we have with T, P as independent variables

$$F_m = U_m - TS_m \qquad 5.\ 04.\ 6$$

$$H_m = U_m + PV_m \qquad 5.\ 04.\ 7$$

$$G_m = U_m - TS_m + PV_m \qquad 5.\ 04.\ 8$$

$$S_m = -\frac{\partial G_m}{\partial T} \qquad 5.\ 04.\ 9$$

$$V_m = \frac{\partial G_m}{\partial P} \qquad 5.\ 04.\ 10$$

$$H_m = G_m - T\frac{\partial G_m}{\partial T} \qquad 5.\ 04.\ 11$$

$$F_m = G_m - P\frac{\partial G_m}{\partial P} \qquad 5.\ 04.\ 12$$

$$U_m = G_m - T\frac{\partial G_m}{\partial T} - P\frac{\partial G_m}{\partial P} \qquad 5.\ 04.\ 13$$

$$C_m = T\frac{\partial S_m}{\partial T} = \frac{\partial H_m}{\partial T} \qquad 5.\ 04.\ 14$$

§ 5. 05 PARTIAL VOLUMES

If we make up a mixture of n_1 units of a substance 1 and n_2 units of a substance 2, then owing to the conservation of mass it is evident that the mass M of the mixture is given by

$$M = n_1 M_1 + n_2 M_2 \qquad\qquad 5.\,05.\,1$$

where M_1 denotes the mass of one unit of the substance 1 and M_2 denotes the mass of one unit of the substance 2. In particular if we choose as unit of quantity the unit of mass then M_1 and M_2 are both equal to this unit of mass. If on the other hand we choose as unit of quantity the mole then M_1, M_2 are the molar masses of the substances 1, 2 respectively.

It would be desirable to have relations similar to (1) for other extensive properties such as the volume V and the entropy S, but since these are usually not conserved on mixing the situation is not so simple. One might define V_1 as having the same value as in the pure substance 1 and then use the relation

$$V = n_1 V_1 + n_2 V_2 \qquad\qquad 5.\,05.\,2$$

as a definition of V_2. But such a convention is repellant owing to the implied dissymmetry with respect to the two species 1 and 2. We accordingly have to proceed by a less obvious path.

We define quantities V_1, V_2 by the relations

$$V_1 = \left(\frac{\partial V}{\partial n_1}\right)_{T,\,P,\,n_2} \qquad\qquad 5.\,05.\,3$$

$$V_2 = \left(\frac{\partial V}{\partial n_2}\right)_{T,\,P,\,n_1} \qquad\qquad 5.\,05.\,4$$

so that for the most general change in a homogeneous mixture of the species 1 and 2 we have

$$dV = \alpha V dT - \varkappa V dP + V_1\,dn_1 + V_2\,dn_2 \qquad\qquad 5.\,05.\,5$$

In particular for variations at constant temperature and pressure we have

$$dV = V_1\,dn_1 + V_2\,dn_2 \qquad \text{(const. } T, P) \qquad 5.\,05.\,6$$

At constant temperature and pressure V is homogeneous of the first degree in n_1, n_2 and so V_1, V_2 are homogeneous of zero degree in n_1, n_2. This means physically that if we increase n_1 and n_2 in the same ratio,

then V is also increased in the same ratio while V_1, V_2 remain constant. If then we consider a variation at constant relative composition, that is to say constant n_1/n_2, we may write

$$\mathrm{d}n_1 = n_1\,\mathrm{d}\xi \qquad \mathrm{d}n_2 = n_2\,\mathrm{d}\xi \qquad \mathrm{d}V = V\mathrm{d}\xi \qquad 5.\,05.\,7$$

Substituting (7) into (6), we obtain

$$V\mathrm{d}\xi = n_1 V_1\,\mathrm{d}\xi + n_2 V_2\,\mathrm{d}\xi \qquad 5.\,05.\,8$$

Now dividing throughout by $\mathrm{d}\xi$ or alternatively integrating from $\xi = 0$ to $\xi = 1$, we obtain

$$V = n_1 V_1 + n_2 V_2 \qquad 5.\,05.\,9$$

which is of the desired form (2). We have thus achieved our object of attaining this relation by means of a symmetrical definition of V_1 and V_2. We call V_1 the *partial volume* of the species 1 and V_2 the *partial volume* of the species 2. These relations are valid whether the unit of quantity is taken to be the unit of mass or the mole.

The above procedure can immediately be extended to mixtures of more than two components. We define partial volumes V_i by

$$V_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,\,P,\,n_j} \qquad 5.\,05.\,10$$

where n_j denotes all the n's except n_i, so that

$$\mathrm{d}V = aV\mathrm{d}T - \varkappa V\mathrm{d}P + \Sigma_i V_i\,\mathrm{d}n_i \qquad 5.\,05.\,11$$

We then deduce from (11) that

$$V = \Sigma_i n_i V_i \qquad 5.\,05.\,12$$

§ 5. 06 OTHER PARTIAL QUANTITIES

Corresponding to any extensive property X the partial quantities X_i are defined precisely as in the case of volume, that is to say

$$X_i = \left(\frac{\partial X}{\partial n_i}\right)_{T,\,P,\,n_j} \qquad 5.\,06.\,1$$

By reasoning precisely analogous to that for volumes we can then deduce

$$X = \Sigma_i n_i X_i \qquad 5.\,06.\,2$$

which for a binary mixture reduces to

$$X = n_1 X_1 + n_2 X_2 \qquad\qquad 5.\,06.\,3$$

It is not necessary to write down relations of this form for each extensive property. It is sufficient to mention as important examples of X the quantities V, S, U, F, H, G, C, C_v.

It is perhaps worth while drawing attention here to the fact that the quantity X need not be a thermodynamic property of the system. It is only required that X shall be an extensive property. We shall merely mention one example of such a non-thermodynamic property. If r denotes the refractive index of a binary mixture, we define the *total refractivity* R of the system by

$$R = \frac{r^2 - 1}{r^2 + 2}\, V \qquad\qquad 5.\,06.\,4$$

so that R is clearly an extensive property. We then define *partial refractivities* in the usual way by

$$R_1 = \left(\frac{\partial R}{\partial n_1}\right)_{T,\,P,\,n_2} \qquad\qquad 5.\,06.\,5$$

$$R_2 = \left(\frac{\partial R}{\partial n_2}\right)_{T,\,P,\,n_1} \qquad\qquad 5.\,06.\,6$$

and it then follows as usual that

$$R = n_1 R_1 + n_2 R_2 \qquad\qquad 5.\,06.\,7$$

The reason for choosing this particular example is the following. There are theoretical grounds for expecting R to be an approximately additive quantity, in which case R_1, R_2 would be independent of the composition of the mixture and have the same values as for the two pure substances. This is more or less supported by experiment. There are however theoretical grounds for expecting in certain cases deviations from simple additivity and this is also confirmed by experiment. The quantitative theoretical discussion of such deviations from simple additivity could be improved by the use of the partial refractivities defined as above.

§ 5. 07 RELATION BETWEEN SEVERAL PARTIAL QUANTITIES

Since the partial quantities are derived from extensive properties by simple differentiation, it follows that they are interrelated in a

manner analogous to the extensive properties from which they are derived. In particular we have, taking T, P as independent variables

$$F_i = U_i - TS_i \qquad \text{5. 07. 1}$$

$$H_i = U_i + PV_i \qquad \text{5. 07. 2}$$

$$G_i = U_i - TS_i + PV_i \qquad \text{5. 07. 3}$$

$$S_i = -\frac{\partial G_i}{\partial T} \qquad \text{5. 07. 4}$$

$$V_i = \frac{\partial G_i}{\partial P} \qquad \text{5. 07. 5}$$

$$H_i = G_i - T\frac{\partial G_i}{\partial T} \qquad \text{5. 07. 6}$$

$$F_i = G_i - P\frac{\partial G_i}{\partial P} \qquad \text{5. 07. 7}$$

$$U_i = G_i - T\frac{\partial G_i}{\partial T} - P\frac{\partial G_i}{\partial P} \qquad \text{5. 07. 8}$$

$$C_i = T\frac{\partial S_i}{\partial T} = \frac{\partial H_i}{\partial T} \qquad \text{5. 07. 9}$$

§ 5. 08 VARIATION OF PARTIAL QUANTITIES WITH COMPOSITION

If we differentiate formula (5. 05. 12) we obtain

$$dV = \Sigma_i n_i\, dV_i + \Sigma_i V_i\, dn_i \qquad \text{5. 08. 1}$$

and comparing this with (5. 05. 11) we deduce

$$-\alpha V dT + \varkappa V dP + \Sigma_i n_i\, dV_i = 0 \qquad \text{5. 08. 2}$$

In particular at constant temperature and pressure we have

$$\Sigma_i n_i\, dV_i = 0 \qquad (\text{const. } T, P) \qquad \text{5. 08. 3}$$

or in the notation introduced in § 5. 03

$$\Sigma_i n_i\, DV_i = 0 \qquad \text{5. 08. 4}$$

Similarly for any other partial quantities X_i we have

$$\Sigma_i n_i\, DX_i = 0 \qquad \text{5. 08. 5}$$

In particular for a binary mixture we have

$$n_1 \frac{\partial X_1}{\partial x} + n_2 \frac{\partial X_2}{\partial x} = 0 \qquad \text{5. 08. 6}$$

§ 5. 09 RELATION BETWEEN PARTIAL QUANTITIES AND MEAN MOLAR OR SPECIFIC QUANTITIES

If we choose as the unit of quantity the mole and we apply the relation (5. 06. 3) to a quantity of a binary mixture containing in all one mole, we obtain

$$X_m = (1 - x) X_1 + x X_2 \qquad \text{5. 09. 1}$$

Similarly applying (5. 08. 6) to one mole of the mixture we have

$$(1 - x) \frac{\partial X_1}{\partial x} + x \frac{\partial X_2}{\partial x} = 0 \qquad \text{5. 09. 2}$$

Differentiating (1) with respect to x we obtain

$$\frac{\partial X_m}{\partial x} = -X_1 + (1 - x) \frac{\partial X_1}{\partial x} + X_2 + x \frac{\partial X_2}{\partial x} \qquad \text{5. 09. 3}$$

Subtracting (2) from (3) we obtain

$$\frac{\partial X_m}{\partial x} = X_2 - X_1 \qquad \text{5. 09. 4}$$

From (1) and (4) we deduce

$$X_1 = X_m - x \frac{\partial X_m}{\partial x} \qquad \text{5. 09. 5}$$

$$X_2 = X_m + (1 - x) \frac{\partial X_m}{\partial x} \qquad \text{5. 09. 6}$$

Formulae (5) and (6) have a simple geometrical interpretation shown in fig. 5. 1. The abscissa is x, increasing from zero at O representing the pure component 1 to unity at O′ representing the pure component 2. Suppose the curve APB to be a plot of the mean molar quantity X_m as ordinate and P to be any point on it. Let the tangent QPR to this curve at P cut the O and O′ ordinates at Q and R respectively. Then from (3) and (4) we see that the partial molar quantities X_1 and X_2 for the composition at P are represented by OQ and O′R respectively. It is clear from this construction or otherwise that for either pure component the partial molar quantity is equal to the mean molar quantity, becoming in fact the molar quantity used in the preceding chapter.

If instead of choosing as unit of quantity the mole we chose the unit of mass, we should obtain instead of (5) and (6)

$$X_1 = X_M \qquad w \frac{\partial X_M}{\partial w} \qquad\qquad 5.09.7$$

$$X_2 = X_M + (1 \qquad w) \frac{\partial X_M}{\partial w} \qquad\qquad 5.09.8$$

where X_M denotes the specific quantity (quantity per unit mass) and w denotes the mass fraction of the substance 2. If then the specific quantity X_M is plotted against the mass fraction w, a construction
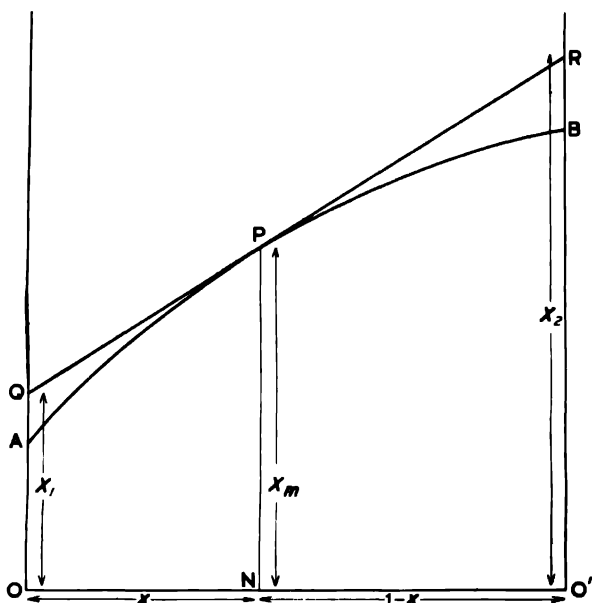

Fig. 5. 1. Relation between partial molar quantities and mean molar quantity.

precisely analogous to that shown in fig. 5. 1 leads to values of the partial quantities X_1 and X_2. The values directly obtained for these partial quantities will be per unit mass and the corresponding values per mole are obtained by multiplication by the molar mass. This procedure for obtaining the partial quantities per mole via the partial quantities per unit mass is convenient especially in the case of volumes, when the information directly available is usually the density, of which the specific volume V_M is the reciprocal, for given values of the mass fraction w.

§ 5.10 PARTIAL QUANTITIES AT HIGH DILUTION

By writing (5. 09. 2) in the form

$$\frac{\partial X_1}{\partial x} \Big/ \frac{\partial X_2}{\partial x} = \frac{x}{1-x} \qquad 5.\,10.\,1$$

we make the interesting observation that as $x \to 0$ either $\dfrac{\partial X_1}{\partial x} \to 0$ or $\dfrac{\partial X_2}{\partial x} \to \infty$. Both alternatives occur. We shall find later that as $x \to 0$, $\dfrac{\partial V_1}{\partial x}, \dfrac{\partial U_1}{\partial x}, \dfrac{\partial H_1}{\partial x}, \dfrac{\partial C_1}{\partial x}$ all tend towards zero, while $\dfrac{\partial S_2}{\partial x}, \dfrac{\partial F_2}{\partial x}, \dfrac{\partial G_2}{\partial x}$ all tend towards infinity.

In the limit $x \to 1$, we of course meet the converse behaviour corresponding to interchange of the species 1 and 2.

§ 5.11 CHEMICAL POTENTIALS AND GIBBS-DUHEM RELATION

All our considerations concerning partial quantities X_i are valid whatever the extensive quantity denoted by X. In particular if we take X to be the Gibbs function G, we have according to the definition (5. 06. 1)

$$G_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,\,P,\,n_j} \qquad 5.\,11.\,1$$

Now from the fundamental relation (1. 31. 6) we have

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,\,P,\,n_j} = \mu_i \qquad 5.\,11.\,2$$

By comparison of (1) and (2) we see that

$$G_i = \mu_i \qquad 5.\,11.\,3$$

When we take X to be G formula (5. 08. 5) becomes

$$\Sigma_i\, n_i\, \mathrm{D}G_i = \Sigma_i\, n_i\, \mathrm{D}\mu_i = 0 \qquad 5.\,11.\,4$$

which is the Gibbs-Duhem relation already derived in § 1. 38, and formula (5. 09. 1) becomes

$$G_m = (1-x)\,\mu_1 + x\mu_2 \qquad 5.\,11.\,5$$

As a consequence of the relation (3) we can derive immediately several important formulae relating to chemical potentials. By

combining (3) with (5. 07. 4), (5. 07. 5), (5. 07. 6), (5. 07. 7) and (5. 07. 8) we obtain

$$S_i = -\frac{\partial \mu_i}{\partial T}$$
　　　5. 11. 6

$$V_i = \frac{\partial \mu_i}{\partial P}$$
　　　5. 11. 7

$$H_i = \mu_i - T\frac{\partial \mu_i}{\partial T}$$
　　　5. 11. 8

$$F_i = \mu_i - P\frac{\partial \mu_i}{\partial P}$$
　　　5. 11. 9

$$U_i = \mu_i - T\frac{\partial \mu_i}{\partial T} - P\frac{\partial \mu_i}{\partial P}$$
　　　5. 11. 10

It follows immediately from (6) and (7) that

$$d\mu_i = -S_i\,dT + V_i\,dP + D\mu_i$$
　　　5. 11. 11

In particular for a binary mixture

$$d\mu_1 = -S_1\,dT + V_1\,dP + \frac{\partial \mu_1}{\partial x}\,dx$$
　　　5. 11. 12

$$d\mu_2 = -S_2\,dT + V_2\,dP + \frac{\partial \mu_2}{\partial x}\,dx$$
　　　5. 11. 13

By combining (3) with (5. 09. 4), (5. 09. 5) and (5. 09. 6) we obtain for a binary mixture

$$\frac{\partial G_m}{\partial x} = \mu_2 - \mu_1$$
　　　5. 11. 14

$$\mu_1 = G_m - x\frac{\partial G_m}{\partial x}$$
　　　5. 11. 15

$$\mu_2 = G_m + (1-x)\frac{\partial G_m}{\partial x}$$
　　　5. 11. 16

We can rewrite the Gibbs-Duhem relation (5) in terms of absolute activities as

$$\Sigma_i\, n_i\, D\ln \lambda_i = 0$$
　　　5. 11. 17

or dividing throughout by $\Sigma_i\, n_i$

$$\Sigma_i\, x_i\, D\ln \lambda_i = 0$$
　　　5. 11. 18

For a binary mixture the Gibbs-Duhem relation reduces to

$$(1 - x) \frac{\partial \mu_1}{\partial x} + x \frac{\partial \mu_2}{\partial x} = 0 \qquad 5.\,11.\,19$$

or alternatively

$$(1 - x) \frac{\partial \ln \lambda_1}{\partial x} + x \frac{\partial \ln \lambda_2}{\partial x} = 0 \qquad 5.\,11.\,20$$

§ 5. 12 BINARY GASEOUS MIXTURES

In considering a mixture of two gases it is convenient to begin with the independent variables T, V and transform to the variables T, P later. We accordingly begin by describing the free energy F.

We recall that for a single gas containing n moles the free energy F is according to (4. 23. 5)

$$F = n\mu^\dagger - nRT + nRT \ln \frac{nRT}{P^\dagger V} + \frac{n^2 RTB}{V} \qquad 5.\,12.\,1$$

neglecting virial coefficients beyond the second. Statistical mechanics shows that the term containing B is due to interactions of pairs of molecules, whereas the higher virial coefficients, which we are neglecting, are connected with simultaneous interactions involving more than two molecules. The remaining terms in (1) are those of a perfect gas in which the molecules are treated as independent.

According to statistical mechanics the extension of (1) to a mixture containing n_1 moles of species 1 and n_2 moles of species 2 is

$$F = n_1 \left\{ \mu_1^\dagger - RT + RT \ln \frac{n_1 RT}{P^\dagger V} \right\}$$

$$+ n_2 \left\{ \mu_2^\dagger - RT + RT \ln \frac{n_2 RT}{P^\dagger V} \right\}$$

$$+ \frac{RT}{V} \left\{ n_1^2 B_{11} + 2n_1 n_2 B_{12} + n_2^2 B_{22} \right\} \qquad 5.\,12.\,2$$

In (2) the term in B_{11} takes account of interactions between pairs of molecules of type 1, B_{22} between pairs of molecules of type 2 and B_{12} between pairs of molecules one of each type. These three coefficients, as well as $\mu_1^\dagger$, $\mu_2^\dagger$ depend only on the temperature. We recall that $P^\dagger$ denotes a standard pressure, the choice of which affects the values of $\mu_1^\dagger$, $\mu_2^\dagger$.

From (2) we derive immediately

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,\,n_1,\,n_2} = (n_1 + n_2)\frac{RT}{V}$$

$$+ \frac{RT}{V^2}\left\{n_1^2 B_{11} + 2n_1 n_2 B_{12} + n_2^2 B_{22}\right\} \qquad 5.\,12.\,3$$

$$\mu_1 = \left(\frac{\partial F}{\partial n_1}\right)_{T,\,V,\,n_2} = \mu_1^\dagger + RT\ln\frac{n_1 RT}{P^\dagger V} + \frac{2RT}{V}\,(n_1 B_{11} + n_2 B_{12})$$
$$5.\,12.\,4$$

$$\mu_2 = \left(\frac{\partial F}{\partial n_2}\right)_{T,\,V,\,n_1} = \mu_2^\dagger + RT\ln\frac{n_2 RT}{P^\dagger V} + \frac{2RT}{V}\,(n_1 B_{12} + n_2 B_{22})$$
$$5.\,12.\,5$$

The absolute activities are given by

$$\ln\lambda_1 = \ln\lambda_1^\dagger + \ln\frac{n_1 RT}{P^\dagger V} + \frac{2}{V}\,(n_1 B_{11} + n_2 B_{12}) \qquad 5.\,12.\,6$$

$$\ln\lambda_2 = \ln\lambda_2^\dagger + \ln\frac{n_2 RT}{P^\dagger V} + \frac{2}{V}\,(n_1 B_{12} + n_2 B_{22}) \qquad 5.\,12.\,7$$

where

$$\lambda_1^\dagger = \exp\,(\mu_1^\dagger/RT) \qquad \lambda_2^\dagger = \exp\,(\mu_2^\dagger/RT) \qquad 5.\,12.\,8$$

§ 5. 13 CHANGE OF VARIABLE FROM V TO P

Formula (5. 12. 3) expresses P as a power series in V^{-1}, which is quadratic because we are neglecting smaller terms of higher order. We can invert this into a formula for V as a power series in P and obtain to the same degree of accuracy

$$\frac{V}{n_1 + n_2} = \frac{RT}{P} + \frac{n_1^2 B_{11} + 2n_1 n_2 B_{12} + n_2^2 B_{22}}{(n_1 + n_2)^2} \qquad 5.\,13.\,1$$

Substituting (1) into (5. 12. 4) we obtain to the same degree of accuracy

$$\mu_1 = \mu_i^\dagger + RT\ln\frac{n_1}{n_1 + n_2} + RT\ln\frac{P}{P^\dagger}$$

$$+ P\left\{B_{11} - \left(\frac{n_2}{n_1 + n_2}\right)^2 (B_{11} - 2B_{12} + B_{22})\right\}$$

$$= \mu_1^\dagger + RT\ln\,(1 - x) + RT\ln\frac{P}{P^\dagger}$$

$$+ P\left\{B_{11} - x^2\,(B_{11} - 2B_{12} + B_{22})\right\} \qquad 5.\,13.\,2$$

where x denotes the mole fraction of species 2. Similarly

$$\mu_2 = \mu_2^\dagger + RT \ln \frac{n_2}{n_1 + n_2} + RT \ln \frac{P}{P^\dagger}$$

$$+ P \left\{ B_{22} - \left(\frac{n_1}{n_1 + n_2}\right)^2 (B_{11} - 2B_{12} + B_{22}) \right\}$$

$$= \mu_2^\dagger + RT \ln x + RT \ln \frac{P}{P^\dagger}$$

$$+ P \left\{ B_{22} - (1 - x)^2 (B_{11} - 2B_{12} + B_{22}) \right\} \qquad 5.\,13.\,3$$

For the absolute activities we have

$$\ln \lambda_1 = \ln \lambda_1^\dagger + \ln \frac{n_1}{n_1 + n_2} + \ln \frac{P}{P^\dagger}$$

$$+ \frac{P}{RT} \left\{ B_{11} - \left(\frac{n_2}{n_1 + n_2}\right) (B_{11} - 2B_{12} + B_{22}) \right. \qquad 5.\,13.\,4$$

$$\ln \lambda_2 = \ln \lambda_2^\dagger + \ln \frac{n_2}{n_1 + n_2} + \ln \frac{P}{P^\dagger}$$

$$+ \frac{P}{RT} \left\{ B_{22} - \left(\frac{n_1}{n_1 + n_2}\right)^2 (B_{11} - 2B_{12} + B_2) \right. \qquad 5.\,13.\,5$$

For the Gibbs function we have

$$G = n_1 \mu_1 + n_2 \mu_2$$

$$= n_1 \mu_1^\dagger + n_2 \mu_2^\dagger + (n_1 + n_2) RT \ln \frac{P}{P^\dagger}$$

$$+ n_1 RT \ln \frac{n_1}{n_1 + n_2} + n_2 RT \ln \frac{n_2}{n_1 + n_2}$$

$$+ P \left\{ n_1 B_{11} + n_2 B_{22} - \frac{n_1 n_2}{n_1 + n_2} (B_{11} - 2B_{12} + B_{22}) \right\} \qquad 5.\,13.\,6$$

For the entropy we have

$$S = -\left(\frac{\partial G}{\partial T}\right)_P = -n_1 \frac{d\mu_1^\dagger}{dT} - n_2 \frac{d\mu_2^\dagger}{dT} - (n_1 + n_2)R \ln \frac{P}{P^\dagger}$$

$$-n_1 R \ln \frac{n_1}{n_1 + n_2} - n_2 R \ln \frac{n_2}{n_1 + n_2}$$

$$-P\left\{ n_1 \frac{dB_{11}}{dT} + n_2 \frac{dB_{22}}{dT} - \frac{n_1 n_2}{n_1 + n_2} \frac{d}{dT}(B_{11} - 2B_{12} + B_{22})\right\} \qquad 5.13.7$$

and for the heat function

$$H = G + TS = n_1\left(\mu_1^\dagger - T\frac{d\mu_1^\dagger}{dT}\right) + n_2\left(\mu_2^\dagger - T\frac{d\mu_2^\dagger}{dT}\right)$$

$$+ Pn_1\left(B_{11} - T\frac{dB_{11}}{dT}\right) + Pn_2\left(B_{22} - T\frac{dB_{22}}{dT}\right)$$

$$- P\frac{n_1 n_2}{n_1 + n_2}\left(1 - T\frac{d}{dT}\right)(B_{11} - 2B_{12} + B_{22}) \qquad 5.13.8$$

The partial molar entropies are

$$S_1 = \left(\frac{\partial S}{\partial n_1}\right)_{T,\,P,\,n_2} = -\left(\frac{\partial \mu_1}{\partial T}\right)_P = -\frac{d\mu_1^\dagger}{dT} - R \ln \frac{n_1}{n_1 + n_2} - R \ln \frac{P}{P^\dagger}$$

$$- P\left\{\frac{dB_{11}}{dT} - \left(\frac{n_2}{n_1 + n_2}\right)^2 \frac{d}{dT}(B_{11} - 2B_{12} + B_{22})\right\}$$

$$= -\frac{d\mu_1^\dagger}{dT} - R \ln (1 - x) - R \ln \frac{P}{P^\dagger}$$

$$- P\left\{\frac{dB_{11}}{dT} - x^2 \frac{d}{dT}(B_{11} - 2B_{12} + B_{22})\right\} \qquad 5.13.9$$

and similarly

$$S_2 = -\frac{d\mu_2^\dagger}{dT} - R \ln x - R \ln \frac{P}{P^\dagger}$$

$$- P\left\{\frac{dB_{22}}{dT} - (1 - x)^2 \frac{d}{dT}(B_{11} - 2B_{12} + B_{22})\right\} \qquad 5.13.10$$

§ 5. 14 PARTIAL PRESSURES AND FUGACITIES

The *partial pressures* p_1 and p_2 are defined by

$$p_1 = \frac{n_1}{n_1 + n_2} P = (1 - x)P \qquad p_2 = \frac{n_2}{n_1 + n_2} P = xP \qquad \text{5. 14. 1}$$

The fugacities p_1^* and p_2^* are defined by

$$\frac{p_1^*}{\lambda_1} = \text{const.} \qquad \frac{p_2^*}{\lambda_2} = \text{const.} \qquad (T \text{ const.}) \qquad \text{5. 14. 2}$$

$$\frac{p_1^*}{p_1} \to 1 \qquad \frac{p_2^*}{p_2} \to 1 \qquad \text{as } P \to 0 \quad (T \text{ const.}) \qquad \text{5. 14. 3}$$

From (1), (2), (3), (5. 13. 4), (5. 13. 5) it follows that

$$\ln p_1^* = \ln p_1 + \frac{P}{RT} \left\{ B_{11} - x^2 \left(B_{11} - 2B_{12} + B_{22} \right) \right\} \qquad \text{5. 14. 4}$$

$$\ln p_2^* = \ln p_2 + \frac{P}{RT} \left\{ B_{22} - (1 - x)^2 \left(B_{11} - 2B_{12} + B_{22} \right) \right\} \qquad \text{5. 14. 5}$$

§ 5. 15 IDEALIZED GASEOUS MIXTURES

The value of B_{12} is usually intermediate between those of B_{11} and B_{22}. Consequently the expression $B_{11} - 2B_{12} + B_{22}$ will often, but not always, be of magnitude small compared with those of B_{11} and B_{22}. It is sometimes assumed in the absence of experimental or theoretical information concerning B_{12} that

$$B_{11} - 2B_{12} + B_{22} = 0 \qquad \text{5. 15. 1}$$

There is no theoretical nor experimental basis in general for (1), which is at best an approximation. The physical assumption which (1) represents is closely allied to the physical assumption which leads to a liquid mixture being ideal in the sense to be defined in § 5. 29. We shall accordingly refer to a binary gaseous mixture assumed to obey (1) as an *idealized mixture*.

For an idealized mixture we deduce from (1) and (5. 12. 3)

$$P = (n_1 + n_2) \frac{RT}{V} + (n_1 + n_2) \frac{RT}{V^2} \left\{ n_1 B_{11} + n_2 B_{22} \right\} \qquad \text{5. 15. 2}$$

Hence the partial pressures defined by (5. 14. 1) are

$$p_1 = n_1 \frac{RT}{V} \left\{ 1 + \frac{n_1 B_{11} + n_2 B_{22}}{V} \right\} \qquad 5.\ 15.\ 3$$

$$p_2 = n_2 \frac{RT}{V} \left\{ 1 + \frac{n_1 B_{11} + n_2 B_{22}}{V} \right\} \qquad 5.\ 15.\ 4$$

whereas according to (5. 14. 4), (5. 14. 5) the fugacities are given by

$$\ln p_1^* = \ln p_1 + \frac{PB_{11}}{RT} \qquad 5.\ 15.\ 5$$

$$\ln p_2^* = \ln p_2 + \frac{PB_{22}}{RT} \qquad 5.\ 15.\ 6$$

According to (5) and (6) the ratio of the fugacity p_1^* to the partial pressure p_1 in the idealized mixture is the same as in the pure single gas at the same total pressure P. This is the empirical relation * often assumed for purposes of calculation. It is equivalent to the assumption (1), which we repeat has in general neither theoretical nor experimental basis.†

§ 5. 16 PERFECT GASEOUS MIXTURE WITH T, V AS VARIABLES

At low pressures it is often allowable to ignore all the terms containing B_{11}, B_{12}, B_{22}. Under these conditions we say that we are regarding the gaseous mixture as *perfect*.

For the free energy of a perfect gaseous binary mixture we have according to (5. 12. 2)

$$F = n_1 \left\{ \mu_1^\dagger - RT + RT \ln \frac{n_1 RT}{P^\dagger V} \right\}$$

$$+ n_2 \left\{ \mu_2^\dagger - RT + RT \ln \frac{n_2 RT}{P^\dagger V} \right\} \qquad 5.\ 16.\ 1$$

Thus the free energy of a perfect gas containing two components is just the sum of the free energies at the same temperature of the two separate gases each occupying the same volume V as the mixture.

This can immediately be extended to a perfect gaseous mixture of more than two species. We then have

$$F = \Sigma_i\, n_i \left\{ \mu_i^\dagger - RT + RT \ln \frac{n_i RT}{P^\dagger V} \right\} \qquad 5.\ 16.\ 2$$

* Lewis and Randall, *Thermodynamics and the Free Energy of Chemical Substances* 1923 p. 226.

† Guggenheim and McGlashan, *Proc. Roy. Soc.* A 1951 **206** 448.

For the entropy we deduce

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,\,n_i} = -\Sigma_i\, n_i \left\{\frac{d\mu_i^\dagger}{dT} + R \ln \frac{n_i\, RT}{P^\dagger V}\right\} \qquad 5.\,16.\,3$$

so that the entropy is the sum of the entropies of each of the separate gases at the same temperature each occupying the same volume V as the mixture.

The energy is given by

$$U = F + TS = \Sigma_i\, n_i \left\{\mu_i^\dagger - T\frac{d\mu_i^\dagger}{dT} - RT\right\} \qquad 5.\,16.\,4$$

from which we see that the energies are at a given temperature both additive and independent of the volume.

The pressure is given by

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,\,n_i} = \Sigma_i\, n_i\, \frac{RT}{V} \qquad 5.\,16.\,5$$

and the partial pressures by

$$p_i = n_i\, \frac{RT}{V} \qquad 5.\,16.\,6$$

We thus see that in a perfect gaseous mixture the partial pressure of each component is the same as if it occupied the same volume at the same temperature in the absence of the other gases. This is *Dalton's law of partial pressures*.

Finally in a perfect gaseous mixture the fugacity is the same as the partial pressure and consequently the condition for equilibrium across a membrane permeable to the species i, but not necessarily to all the other species, becomes

$$p_i^a = p_i^\beta \qquad 5.\,16.\,7$$

where the superscripts a, β refer to the two sides of the membrane.

§ 5. 17 PERFECT GASEOUS MIXTURE WITH T, P AS VARIABLES

If we wish to use the independent variables T, P we must return to the formulae of § 5. 13. Omitting all terms containing B_{11}, B_{12} and the like we obtain as formulae for a perfect gaseous mixture

$$G = \Sigma_i\, n_i \left\{\mu_i^\dagger + RT \ln \frac{P}{P^\dagger} + RT \ln \frac{n_i}{\Sigma_k\, n_k}\right\} \qquad 5.\,17.\,1$$

$$\mu_i = \mu_i^\dagger + RT \ln \frac{P}{P^\dagger} + RT \ln \frac{n_i}{\Sigma_k n_k}$$

$$= \mu_i^\dagger + RT \ln \frac{P}{P^\dagger} + RT \ln x_i$$

$$= \mu_i^\dagger + RT \cdot \ln \frac{p_i}{P^\dagger} \qquad\qquad 5.17.2$$

$$\lambda_i = \lambda_i^\dagger \frac{p_i}{P^\dagger} \qquad\qquad 5.17.3$$

$$S = \Sigma_i \, n_i \left\{ -\frac{d\mu_i^\dagger}{dT} - R \ln \frac{P}{P^\dagger} - R \ln \frac{n_i}{\Sigma_k n_k} \right.$$

$$= \Sigma_i \, n_i \left\{ -\frac{d\mu_i^\dagger}{dT} - R \ln \frac{p_i}{P^\dagger} \right\} \qquad\qquad 5.17.4$$

Whereas we saw in the preceding section that the thermodynamic functions of a perfect gaseous mixture are additive at given T, V we see that this is by no means the case at given T, P. The entropy contains the extra terms

$$-R \, \Sigma_i \, n_i \ln \frac{n_i}{\Sigma_k n_k} = -R \, \Sigma_i \, n_i \ln x_i \qquad\qquad 5.17.5$$

usually called the *entropy of mixing*. The same extra terms occur in J and Y. Correspondingly G and F contain the extra terms

$$RT \, \Sigma_i \, n_i \ln \frac{n_i}{\Sigma_k n_k} = RT \, \Sigma_i \, n_i \ln x_i \qquad\qquad 5.17.6$$

We also note the interesting result that in a perfect gaseous mixture each μ_i can be expressed as a function of temperature and partial pressure p_i independent of the total pressure and of the partial pressures of the other species.

The volume, the heat function and the energy are given by

$$V = \frac{\partial G}{\partial P} = \Sigma_i \, n_i \frac{RT}{P} \qquad\qquad 5.17.7$$

$$H = G + TS = \Sigma_i \, n_i \left(\mu_i^\dagger - T \frac{d\mu_i^\dagger}{dT} \right) \qquad\qquad 5.17.8$$

$$U = H - PV = \Sigma_i \, n_i \left(\mu_i^\dagger - T \frac{d\mu_i^\dagger}{dT} - RT \right) \qquad\qquad 5.17.9$$

For the partial molar quantities other than the G_i, which are the same as the μ_i, we have

$$S_i = \frac{\partial S}{\partial n_i} = -\frac{\partial \mu_i}{\partial T} = -\frac{d\mu_i^\dagger}{dT} - R \ln \frac{P}{P^\dagger} - R \ln \frac{n_i}{\Sigma_k n_k}$$

$$= -\frac{d\mu_i}{dT} - R \ln \frac{p_i}{P^\dagger} \qquad 5.\,17.\,10$$

$$V_i = \frac{\partial V}{\partial n_i} = \frac{RT}{P} \qquad 5.\,17.\,11$$

$$H_i = G_i + TS_i = \mu_i^\dagger - T\frac{d\mu_i^\dagger}{dT} = -RT^2\frac{d\ln\lambda_i^\dagger}{dT} \qquad 5.\,17.\,12$$

$$U_i = H_i - PV_i = \mu_i^\dagger - T\frac{d\mu_i^\dagger}{dT} - RT \qquad 5.\,17.\,13$$

From (12) and (13) it follows that the partial molar heat capacities are equal to the molar heat capacities of the pure components.

§ 5. 18 INTRODUCTION TO BINARY LIQUIDS

We now turn to liquid mixtures and the equilibrium between such phases and other phases, especially a gas phase. We begin by certain general considerations applying to all such liquid mixtures. We shall next consider a special class of such mixtures, called *ideal*, which exhibit an especially simple behaviour. We shall then show how the behaviour of non-ideal mixtures can conveniently be compared and correlated with that of ideal mixtures. The procedure will be illustrated in greater detail for a class of mixtures called *simple*.

§ 5. 19 ABSOLUTE ACTIVITIES, RELATIVE ACTIVITIES AND FUGACITIES

All the equilibrium properties of each species i are determined by its chemical potential μ_i, or its absolute activity λ_i related to μ_i by the definition *

$$\mu_i = RT \ln \lambda_i \qquad 5.\,19.\,1$$

Up to the present we have mentioned absolute activities from time to time and have given formulae for them with the object of familiarizing the reader with them. We have however hitherto made little

* Fowler and Guggenheim, *Statistical Thermodynamics* 1939 p. 66.

use of absolute activities. Henceforth we shall make considerably increasing use of them, for in the treatment of mixtures they are often more convenient than chemical potentials.

In our consideration of liquid mixtures we shall be particularly concerned with a comparison of the equilibrium properties of the mixture with those of the pure components. Consequently we shall be concerned not so much with μ_i itself as with the difference $\mu_i - \mu_i^0$ where the superscript ^{0} denotes the value for the pure liquid at the same temperature and pressure. From (1) we have

$$\mu_i - \mu_i^0 = RT \ln \frac{\lambda_i}{\lambda_i^0} \qquad 5.\ 19.\ 2$$

where the superscript ^{0} is used again with the same meaning. We shall be particularly concerned with the ratios λ_i/λ_i^0. These ratios are called *relative activities* and will be denoted by a_i. This name and this symbol are due to G. N. Lewis *. We have then

$$\mu_i - \mu_i^0 = RT \ln a_i \qquad 5.\ 19.\ 3$$

We must mention that other quantities than the relative activities defined here are sometimes also called activities and are denoted by the same symbol a_i. In order to avoid confusion we shall make no use or further mention of such other quantities.

For the equilibrium of the species i between any two phases α and β we have according to (4. 15. 7) the simple condition

$$\lambda_i^\alpha = \lambda_i^\beta \qquad 5.\ 19.\ 4$$

and in particular for the equilibrium between a liquid phase L and a gas phase G

$$\lambda_i^L = \lambda_i^G \qquad 5.\ 19.\ 5$$

From (5) and (5. 14. 2) it follows that the ratio of the absolute activities of the species i in any two liquid phases α, β is equal to the ratio of the fugacities of the species in the gas phases in equilibrium with α, β respectively.

We now define the *fugacity* p_i^* of a species i in any phase, liquid or otherwise, as equal to the fugacity of this species in the gas phase in equilibrium with the phase considered. We then have for the species i in any two phases α and β

$$\frac{\lambda_i^\alpha}{\lambda_i^\beta} = \frac{p_i^{*\alpha}}{p_i^{*\beta}} \qquad 5.\ 19.\ 6$$

* Lewis, *J Amer Chem Soc.* 1913 **35** 17

If the pressure in the gas phase is low we may often treat the gas as perfect. The fugacities p_i^* then become equal to the partial pressures p_i. According to this approximation (6) reduces to

$$\frac{\lambda_i^a}{\lambda_i^\beta} = \frac{p_i^a}{p_i^\beta} \qquad 5.\,19.\,7$$

An important application of (6) is to the comparison between the absolute activity λ_i of i in a liquid mixture and its absolute activity λ_i^0 in the pure liquid at the same temperature and pressure. We then have

$$a_i = \frac{\lambda_i}{\lambda_i^0} = \frac{p_i^*}{p_i^{*0}} \qquad 5.\,19.\,8$$

or if we treat the gas as perfect

$$a_i = \frac{\lambda_i}{\lambda_i^0} = \frac{p_i}{p_i^0} \qquad 5.\,19.\,9$$

Formula (8), or its approximation (9) expresses the relative activity a_i in terms of experimentally determinable quantities p_i^*, p_i^{*0} or p_i, p_i^0.

§ 5. 20 CONVENTION RELATING TO FUGACITIES

For the sake of brevity and simplicity we shall henceforth, except when stated to the contrary, treat all vapours as perfect gases. We shall accordingly throughout assume in accordance with (5. 19. 9)

$$a_i = \frac{\lambda_i}{\lambda_i^0} = \frac{p_i}{p_i^0} \qquad 5.\,20.\,1$$

If ever the approximation of treating the vapours as perfect gases is not adequate, it is merely necessary to replace the partial vapour pressures p_i by the fugacities p_i^*.

We shall sometimes require (1) in the differential form

$$\mathrm{d}\ln a_i = \mathrm{d}\ln \lambda_i = \mathrm{d}\ln p_i \qquad (\text{const. } T) \qquad 5.\,20.\,2$$

§ 5. 21 DUHEM-MARGULES RELATION

We recall that the Gibbs-Duhem relation in the notation defined in § 5. 03 takes the form (5. 11. 5)

$$\Sigma_i\, n_i\, \mathrm{D}\mu_i = 0 \qquad 5.\,21.\,1$$

or the form (5. 11. 17)

$$\Sigma_i\, n_i\, \mathrm{D}\ln \lambda_i = 0 \qquad 5.\,21.\,2$$

From (5. 20. 2) and (2) we deduce

$$\Sigma_i \, n_i \, \mathrm{D} \ln p_i = 0 \qquad\qquad 5.\,21.\,3$$

or dividing by $\Sigma_i \, n_i$

$$\Sigma_i \, x_i \, \mathrm{D} \ln p_i = 0 \qquad\qquad 5.\,21.\,4$$

This important relation is known as the *Duhem-Margules relation*.*

In the simple case of a binary mixture (4) reduces to

$$(1 - x)\,\frac{\partial \ln p_1}{\partial x} + x\,\frac{\partial \ln p_2}{\partial x} = 0 \qquad\qquad 5.\,21.\,5$$

where as usual x denotes the mole fraction of species 2. It follows from this relation that if p_1 and p_2 are plotted against x, the shape of either
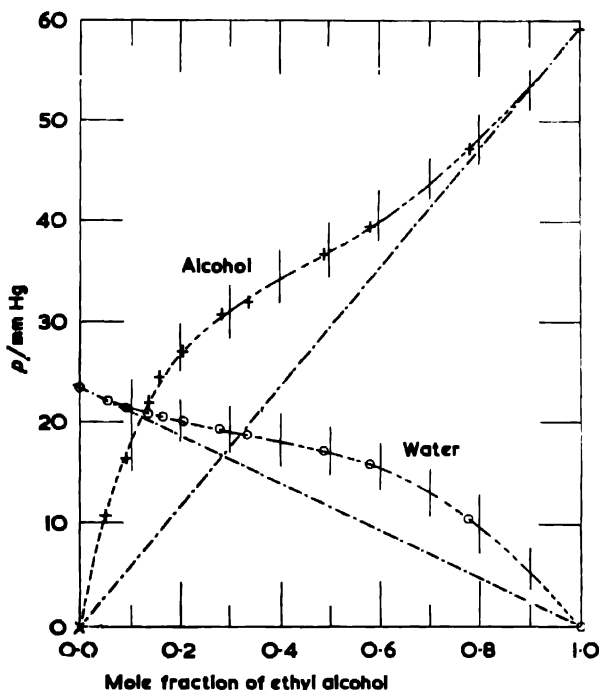
Fig. 5. 2. Illustration of Duhem-Margules relation.

curve completely determines the shape of the other. An example of this interrelation † between the pair of curves is shown in fig. 5. 2 and table 5. 1, where the subscript $_1$ denotes water and $_2$ denotes ethyl alcohol.

* Margules, *S.B. Akad. Wiss. Wien* 1895 **104** 1258—1260.
† See Adam and Guggenheim, *Proc. Roy. Soc. A.* 1933 **139** 231.

TABLE 5. 1
Verification of Duhem-Margules relation for mixtures
of water and ethyl alcohol at 25 °C

x	$\dfrac{p_1}{\text{mm Hg}}$	$\dfrac{p_2}{\text{mm Hg}}$	$-(1-x)\dfrac{\partial \ln p_1}{\partial x}$ $= x\dfrac{\partial \ln p_2}{\partial x}$
0	23 75	0.0	1.00
0 1	21.7	17 8	0.76
0.2	20 4	26.8	0.41
0.3	19 4	31.2	0.37
0.4	18.35	34.2	0 355
0.5	17 3	36.9	0.41
0.6	15.8	40 1	0.53
0.7	13 3	43.9	0 655
0.8	10 0	48.3	0.77
0.9	5 5	53.3	0 915
1.0	0 0	59 0	1.00

§ 5. 22 PRESSURE DEPENDENCE

The fundamental equation (1. 33. 4) can be rewritten in terms of absolute activities as

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \Sigma_i\, RT \ln \lambda_i\, \mathrm{d}n_i \qquad 5.\,22.\,1$$

By applying the cross differentiation identity (3. 01. 7) we deduce, using the definition (5. 05. 10) of V_i,

$$RT\frac{\partial \ln \lambda_i}{\partial P} = \frac{\partial}{\partial P}\frac{\partial G}{\partial n_i} = \frac{\partial}{\partial n_i}\frac{\partial G}{\partial P} = \frac{\partial V}{\partial n_i} = V_i \qquad 5.\,22.\,2$$

and consequently, using (5. 20. 2)

$$\frac{\partial \ln p_i}{\partial P} = \frac{\partial \ln \lambda_i}{\partial P} = \frac{V_i}{RT} \qquad 5.\,22.\,3$$

Neglecting compressibility, which is justifiable for any liquid phase at ordinary pressures, and integrating (3) we obtain

$$\ln \frac{p_i\,(P)}{p_i\,(0)} = \ln \frac{\lambda_i\,(P)}{\lambda_i\,(0)} = \frac{PV_i}{RT} \qquad 5.\,22.\,4$$

Just as for a pure liquid $PV_i \ll RT$ even at pressures of several atmospheres. Consequently for pressures not exceeding about one atmosphere

we may with sufficient accuracy regard λ_i and p_i as independent of the pressure P.

We shall accordingly usually neglect the dependence of the absolute activity λ_i and the vapour pressure p_i in the liquid mixture on the total pressure P, except when we are particularly interested in high values of P as when we come to consider osmotic equilibrium in § 5. 27.

Although the effect of varying the total pressure on a liquid phase is usually negligible, it is important to clarify what exactly we mean by such an effect. In theory the total pressure on a condensed phase in equilibrium with saturated vapour might be varied by separating the liquid from the vapour by a piston permeable to the vapour but not to the liquid. Such an arrangement has however little practical importance, but in practice an analogous result is obtainable by addition to the gas phase of an inert gas insoluble in the liquid. For we have seen in § 5. 17 that in a perfect gaseous mixture the absolute activity of each species is at a given temperature determined completely by its partial pressure and is unaffected by the partial pressures of the other species. Consequently if we add an inert gas insoluble in the liquid, this may be regarded not as a component of the system under discussion, but merely as part of the apparatus used to fix the pressure on the liquid phase. What has just been said applies to a pure liquid as well as to a liquid mixture.

§ 5. 23 EQUILIBRIUM BETWEEN LIQUID AND VAPOUR

Let us now consider from a very general point of view the equilibrium conditions between a liquid mixture of c species and a vapour phase. Each phase by itself has evidently $c + 1$ degrees of freedom, which we can take as given by the $c + 1$ independent variables $T, P, x_2, x_3, \ldots x_c$. Alternatively if we use the $c + 2$ variables $T, P, \mu_1, \mu_2, \ldots \mu_c$ these are not independent being connected by the Gibbs-Duhem relation

$$S dT - V dP + n_1\, d\mu_1 + n_2\, d\mu_2 + \ldots + n_c\, d\mu_c = 0 \qquad 5.\ 23.\ 1$$

If we now consider two phases, one liquid and the other vapour, in mutual equilibrium then the variables $T, P, \mu_1, \mu_2, \ldots \mu_c$ are connected by two Gibbs-Duhem relations, one for each phase. Thus, using the superscripts ^{L} to denote liquid and ^{G} to denote gas, we have

$$S^L\, dT - V^L\, dP + n_1^L\, d\mu_1 + n_2^L\, d\mu_2 + \ldots + n_c^L\, d\mu_c = 0 \qquad 5.\ 23.\ 2$$

$$S^G\, dT - V^G\, dP + n_1^G\, d\mu_1 + n_2^G\, d\mu_2 + \ldots + n_c^G\, d\mu_c = 0 \qquad 5.\ 23.\ 3$$

The term $-V^{L}\,\mathrm{d}P$ in (2) is, as explained in the previous section, usually negligible, but in the present context nothing is gained by its omission.

It is convenient to rewrite (2) and (3) in terms of a single mole of each phase. Thus

$$S_m^{L}\,\mathrm{d}T - V_m^{L}\,\mathrm{d}P + x_1^{L}\,\mathrm{d}\mu_1 + x_2^{L}\,\mathrm{d}\mu_2 + \ldots + x_c^{L}\,\mathrm{d}\mu_c = 0 \qquad 5.\,23.\,4$$

$$S_m^{G}\,\mathrm{d}T - V_m^{G}\,\mathrm{d}P + x_1^{G}\,\mathrm{d}\mu_1 + x_2^{G}\,\mathrm{d}\mu_2 + \ldots + x_c^{G}\,\mathrm{d}\mu_c = 0 \qquad 5.\,23.\,5$$

It is hardly necessary to point out that we need not attach superscripts to the variables $T, P, \mu_1, \mu_2, \ldots \mu_c$ since at equilibrium each of these has the same value in both phases.

From (4) and (5) we could, if we wished, eliminate any one of the quantities $\mathrm{d}T,\ \mathrm{d}P,\ \mathrm{d}\mu_1,\ \mathrm{d}\mu_2, \ldots \mathrm{d}\mu_c$ thus obtaining a single relation between the remaining $c + 1$ quantities. Whether we do this or not, it is clear that only c of these quantities are independent. We conclude that a system of two phases and c component species in equilibrium has c degrees of freedom.

§ 5. 24 GIBBS' PHASE RULE

The discussion in the previous section of the number of degrees of freedom in a system of two phases in readily extended to a system of more than two phases. If we use the $c + 2$ variables $T, P, \mu_1, \mu_2, \ldots \mu_c$ and there are p phases in mutual equilibrium there will be p Gibbs-Duhem relations between the variables. Consequently the number of independent variables or the number of degrees of freedom of the system is $c + 2 - p$. This is *Gibbs' phase rule*.

We have implicitly excluded chemical reaction between the species and we postpone discussion of the effect of any such complication to chapter 7.

§ 5. 25 BINARY AZEOTROPIC MIXTURES

For a binary liquid-vapour system the relations (5.23.4) and (5.23.5) reduce to

$$S_m^{L}\,\mathrm{d}T - V_m^{L}\,\mathrm{d}P + (1 - x^{L})\,\mathrm{d}\mu_1 + x^{L}\,\mathrm{d}\mu_2 = 0 \qquad 5.\,25.\,1$$

$$S_m^{G}\,\mathrm{d}T - V_m^{G}\,\mathrm{d}P + (1 - x^{G})\,\mathrm{d}\mu_1 + x^{G}\,\mathrm{d}\mu_2 = 0 \qquad 5.\,25.\,2$$

where as usual x^{L}, x^{G} denote mole fractions of the second species. If we subtract (1) from (2) we obtain

$$(S_m^{G} - S_m^{L})\,\mathrm{d}T - (V_m^{G} - V_m^{L})\,\mathrm{d}P + (x^{L} - x^{G})\,(\mathrm{d}\mu_1 - \mathrm{d}\mu_2) = 0 \qquad 5.\,25.\,3$$

We shall show that this leads to particularly simple and interesting results when the relative compositions of the two phases are the same that is to say when

$$x^L = x^G \qquad \qquad 5.\,25.\,4$$

Such mixtures are called *azeotropic*, which means that their composition is not changed by boiling.

Let us first consider variations of pressure and composition at constant temperature. Then (3) becomes

$$(V_m^G - V_m^L)\frac{dP}{dx} = (x^L - x^G)\left(\frac{\partial \mu_1}{\partial x} - \frac{\partial \mu_2}{\partial x}\right) \qquad \text{(const. } T) \qquad 5.\,25.\,5$$

Hence for an azeotropic mixture, according to (4)

$$(V_m^G - V_m^L)\frac{dP}{dx} = 0 \qquad \text{(const. } T) \qquad 5.\,25.\,6$$

and since $V_m^G \neq V_m^L$ it follows that

$$\frac{dP}{dx} = 0 \qquad \text{(const. } T) \qquad 5.\,25.\,7$$

This tells us that at a given temperature the total vapour pressure of a binary liquid mixture is a maximum or a minimum at the composition of the azeotropic mixture.

Similarly if we consider variations of temperature and composition at constant pressure, then (3) becomes

$$-(S_m^G - S_m^L)\frac{dT}{dx} = (x^L - x^G)\left(\frac{\partial \mu_1}{\partial x} - \frac{\partial \mu_2}{\partial x}\right) \qquad \text{(const. } P) \qquad 5.\,25.\,8$$

and consequently for an azeotropic mixture

$$(S_m^G - S_m^L)\frac{dT}{dx} = 0 \qquad \text{(const. } P) \qquad 5.\,25.\,9$$

Since $S_m^G \neq S_m^L$, it follows that

$$\frac{dT}{dx} = 0 \qquad \text{(const. } P) \qquad 5.\,25.\,10$$

This tells us that at a given pressure the boiling temperature of a binary liquid mixture is a maximum or a minimum at the composition of the azeotropic mixture.

These striking conclusions seem quite natural when expressed by diagrams. For example fig. 5. 3 shows the boiling point T plotted against compositions of the two phases. For instance the points L and
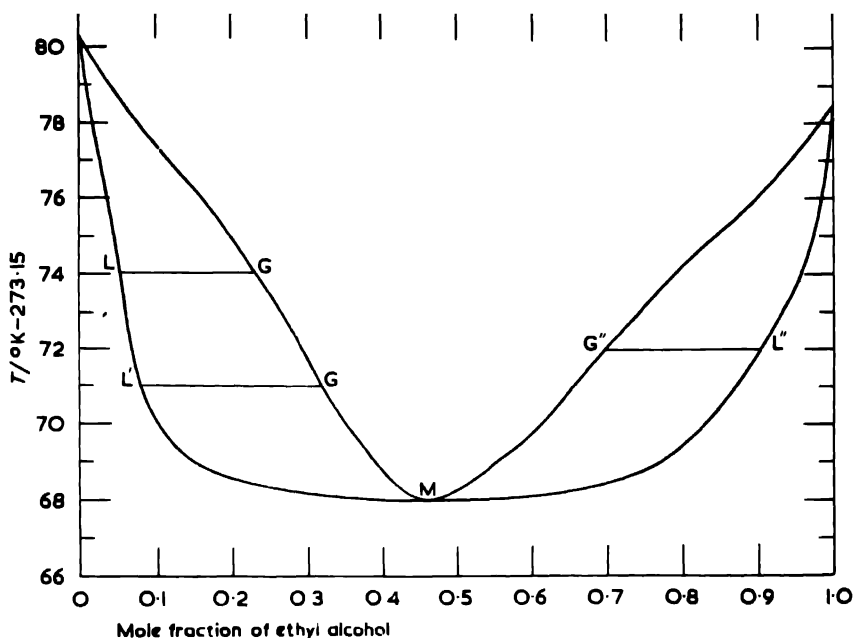
Fig. 5. 3. Boiling point of mixtures of benzene and ethyl alcohol at one atmosphere.

G represent the liquid and gas phases in equilibrium at one temperature; L', G' is another such pair and L", G" another. The point M represents liquid and gas of the same composition and in this example the equilibrium temperature or boiling point is a minimum.

Let us now consider simultaneous variation of temperature and pressure such that the mixture remains azeotropic. Returning to formula (3) and substituting the condition for azeotropy (4), we have

$$(S_m^G - S_m^L)\, dT - (V_m^G - V_m^L)\, dP = 0 \qquad 5.\,25.\,11$$

which we can rewrite as

$$\frac{dP}{dT} = \frac{S_m^G - S_m^L}{V_m^G - V_m^L} = \frac{\Delta_e S}{\Delta_e V} \qquad 5.\,25.\,12$$

of the same form as Clapeyron's relation (4. 41. 7).

§ 5. 26 TEMPERATURE COEFFICIENTS

The fundamental equation (1. 33. 14) can be rewritten in terms of absolute activities as

$$dY = \frac{H}{T^2} dT - \frac{V}{T} dP - R \, \Sigma_i \ln \lambda_i \, dn_i \qquad 5.\,26.\,1$$

Applying the cross-differentiation identity (3. 01. 7) we deduce, using the definition of partial heat function H_i in § 5. 06,

$$-R \frac{\partial \ln \lambda_i}{\partial T} = \frac{\partial}{\partial T} \frac{\partial Y}{\partial n_i} = \frac{\partial}{\partial n_i} \frac{\partial Y}{\partial T} = \frac{1}{T^2} \frac{\partial H}{\partial n_i} = \frac{H_i}{T^2} \qquad 5.\,26.\,2$$

and consequently using (5. 20. 2)

$$\frac{\partial \ln p_i}{\partial T} = \frac{\partial \ln \lambda_i}{\partial T} = \frac{H_i}{RT^2} \qquad 5.\,26.\,3$$

If we apply (3) to a liquid mixture and to the pure liquid 1 and subtract we obtain

$$\frac{\partial \ln (p_i/p_i^0)}{\partial T} = \frac{\partial \ln a_i}{\partial T} = -\frac{H_i - H_i^v}{RT^2} \qquad 5.\,26.\,4$$

§ 5. 27 OSMOTIC EQUILIBRIUM

Suppose we have two liquid mixtures α and β separated by a membrane permeable to the species 1 but impermeable to all other species present in either mixture. In this connection we shall follow the customary practice of calling the permeant species 1 the *solvent* and the nonpermeant species *solutes*. We assume that the two phases are at the same temperature, but not necessarily at the same pressure. The condition that the two phases should be in equilibrium with respect to the solvent species 1 is

$$\lambda_1^a = \lambda_1^\beta \qquad 5.\,27.\,1$$

or if we use (5. 20. 1)

$$p_1^a = p_1^\beta \qquad 5.\,27.\,2$$

For these relations to be satisfied it will generally be necessary for the two phases to be at different pressures. There is then equilibrium with respect to the solvent species 1, but not with respect to the solute species nor is there hydrostatic equilibrium between the two phases, the difference of pressure being balanced by a force exerted by the

membrane. A partial equilibrium of this kind is called *osmotic equilibrium* of the solvent species 1.

By using the relation (5. 22. 3)

$$\frac{\partial \ln p_1}{\partial P} = \frac{\partial \ln \lambda_1}{\partial P} = \frac{V_1}{RT} \qquad 5.\ 27.\ 3$$

we can determine the pressure difference $P^a - P^\beta$ required to preserve osmotic equilibrium.

We shall use the notation $p_1 (P, x)$ to denote the value of the partial vapour pressure p_1 in a phase of composition x at a pressure P. We do not refer to the temperature as this is assumed constant throughout. The condition (2) for osmotic equilibrium becomes in this notation

$$p_1 (P^a, x^a) = p_1 (P^\beta, x^\beta) \qquad 5.\ 27.\ 4$$

Dividing both sides of (4) by $p_1 (P^\beta, x^a)$ and taking logarithms, we obtain

$$\ln \frac{p_1 (P^a, x^a)}{p_1 (P^\beta, x^a)} = \ln \frac{p_1 (P^\beta, x^\beta)}{p_1 (P^\beta, x^a)} \qquad 5.\ 27.\ 5$$

If we integrate (3) from P^β to P^a and substitute the result on the left side of (5) we find

$$\frac{1}{RT} \int_{P^\beta}^{P^a} V_1^a \, dP = \ln \frac{p_1 (P^\beta, x^\beta)}{p_1 (P^\beta, x^a)} \qquad 5.\ 27.\ 6$$

In order to evaluate the integral in (6) it is for most purposes sufficient to ignore compressibility and treat V_1 as independent of P. In case greater refinement should be desired, we can obtain all the accuracy that can ever be required by assuming that V_1 varies linearly with P. We then obtain

$$\frac{[V_1^a]}{RT} (P^a - P^\beta) = \ln \frac{p_1 (P^\beta, x^\beta)}{p_1 (P^\beta, x^a)} \qquad 5.\ 27.\ 7$$

where the symbol $[V_1^a]$ denotes the value of V_1^a at a pressure equal to the mean of P^a and P^β.

Formula (7) is the general relation determining the pressure difference across the membrane at osmotic equilibrium. The case of greatest interest is when the phase β consists of the pure solvent. The pressure difference $P^a - P^\beta$ is then called the *osmotic pressure* and is denoted

by Π. We can in this case replace the superscript $^\beta$ by ^{0} and drop the superscript $^\alpha$. We thus have

$$\frac{\Pi[V_1]}{RT} = \ln \frac{p_1^0(P)}{p_1(P)}$$ 5. 27. 8

or if, as is often the case, we may ignore compressibility

$$\frac{\Pi V_1}{RT} = \ln \frac{p_1^0(P)}{p_1(P)}$$ 5. 27. 9

If moreover the pressure P on the pure solvent is roughly atmospheric, then regardless of how great Π may be we may as explained i[r] § 5. 22 regard p_1 and p_1^0 as essentially independent of P. Formula (9) can then be simplified to

$$\frac{\Pi V_1}{RT} = \ln \frac{p_1^0}{p_1}$$ 5. 27. 10

from which we see that provided the pressure P on the pure solvent is low, the osmotic pressure Π does not depend significantly on P.

If instead of dividing both sides of (4) by $p_1(P^\beta, x^\alpha)$, we divide both sides by $p_1(P^\alpha, x^\beta)$ and otherwise proceed in the same way, we obtain instead of (7)

$$\frac{[V_1^\beta]}{RT}(P^\alpha - P^\beta) = \ln \frac{p_1(P^\alpha, x^\beta)}{p_1(P^\alpha, x^\alpha)}$$ 5. 27. 11

and instead of (8)

$$\frac{\Pi[V_1^0]}{RT} = \ln \frac{p_1^0(P + \Pi)}{p_1(P + \Pi)}$$ 5. 27. 12

It can be shown that the alternative formulae (8) and (12) are fully equivalent. On the whole formula (8) is the more useful.

§ 5. 28 PRESSURE ON SEMI-PERMEABLE MEMBRANE

The osmotic pressure is by definition a pressure that must be applied to the solution to bring it into a certain equilibrium condition. It is not a pressure exerted by the solution or part of the solution at its normal low pressure. It is, in fact, analogous to the freezing point of a solution, which has no relation to the actual temperature of the solution, but is the temperature to which it must be brought to reach a certain equilibrium state. The osmotic pressure is nevertheless sometimes

defined as the pressure exerted on a membrane, permeable only to the solvent, separating the solution from pure solvent. This definition, unless carefully qualified, is incorrect. Another definition sometimes given is the pressure exerted by the solute molecules on a membrane permeable only to the solvent. This definition is still more incorrect than the last. The truth as regards the pressure on the membrane is as follows. When the solution is at the same pressure, e.g. atmospheric, as the solvent, there will be a resultant flow of solvent through the membrane from the solvent to the solution, but the resultant pressure on the membrane itself is negligibly small, and may be in either direction. If, however, the solution is subjected to a certain high external pressure, the flow of solvent through the membrane is equal in either direction; there is then osmotic equilibrium and the excess pressure on the solution over the pressure of the solvent is by definition the osmotic pressure. Under conditions of osmotic equilibrium, but only under these conditions, is the external pressure difference required to prevent the membrane from moving equal to the osmotic pressure.

§ 5. 29 IDEAL MIXTURES

In order to obtain more detailed information concerning the equilibrium properties of liquid mixtures it is necessary to know or assume something about the dependence of the chemical potentials μ_i or the absolute activities λ_i on the composition of the mixture. Thermodynamic considerations alone cannot predict the form of this dependence, but only impose certain restrictions such as the Gibbs-Duhem relation.

We shall begin by considering liquid mixtures having the property that at constant temperature and pressure the dependence of the Gibbs function G, and consequently also of functions derived from G, on the composition is of the same form as for a perfect gaseous mixture. This means that the value of G in a mixture containing n_i moles of the species i exceeds the value of G for the unmixed species at the same temperature and pressure by the negative amount

$$\Delta G = RT \, \Sigma_i \, n_i \ln \frac{n_i}{\Sigma_k \, n_k} \qquad \text{5. 29. 1}$$

Such mixtures are called *ideal mixtures*. We shall devote considerable attention to such mixtures for several reasons.

In the first place the behaviour of ideal mixtures is the simplest conceivable either from a mathematical or from a physical aspect.

In the second place statistical theory predicts that mixtures of very similar species, in particular isotopes, will be ideal.

In the third place it is found experimentally that ideal or almost ideal mixtures do exist, for example benzene and bromobenzene; another example is ethylene bromide and propylene bromide.

In the fourth place although most real mixtures are not ideal, in many cases the resemblances between a real mixture and an ideal mixture are more striking than the differences.

§ 5. 30 THERMODYNAMIC FUNCTIONS OF IDEAL MIXTURES

From formula (5. 29. 1) we can immediately derive formulae for all the thermodynamic functions of an ideal mixture. In particular we have, using the superscript ^{0} to refer to the pure liquids

$$\mu_i = RT \ln \lambda_i = \frac{\partial G}{\partial n_i} = \mu_i^0 + RT \ln \frac{n_i}{\Sigma_k n_k} = \mu_i^0 + RT \ln x_i \qquad 5.\,30.\,1$$

$$a_i = \frac{\lambda_i}{\lambda_i^0} = x_i \qquad 5.\,30.\,2$$

$$G_m = \Sigma_i x_i \mu_i = \Sigma_i x_i \mu_i^0 + RT \Sigma_i x_i \ln x_i \qquad 5.\,30.\,3$$

$$Y_m = -R \Sigma_i x_i \ln \lambda_i^0 - R \Sigma_i x_i \ln x_i \qquad 5.\,30.\,4$$

$$S_m = -\Sigma_i x_i \frac{\partial \mu_i^0}{\partial T} - R \Sigma_i x_i \ln x_i \qquad 5.\,30.\,5$$

$$H_m = \Sigma_i x_i \left(\mu_i^0 - T \frac{\partial \mu_i^0}{\partial T} \right) = \Sigma_i x_i H_i^0 \qquad 5.\,30.\,6$$

$$V_m = \Sigma_i x_i \frac{\partial \mu_i^0}{\partial P} = \Sigma_i x_i V_i^0 \qquad 5.\,30.\,7$$

$$S_i = -\frac{\partial \mu_i^0}{\partial T} - R \ln x_i \qquad 5.\,30.\,8$$

$$H_i = \mu_i^0 - T \frac{\partial \mu_i^0}{\partial T} = H_i^0 \qquad 5.\,30.\,9$$

$$V_i = \frac{\partial \mu_i^0}{\partial P} = V_i^0 \qquad 5.\,30.\,10$$

Furthermore if we use the symbol Δ_m to denote the increase in a

function when one mole of mixture is formed from the pure component species at constant temperature and pressure we have

$$\Delta_m G = RT \Sigma_i x_i \ln x_i \qquad\qquad 5.\ 30.\ 11$$

$$\Delta_m S = -R \Sigma_i x_i \ln x_i \qquad\qquad 5.\ 30.\ 12$$

$$\Delta_m H = 0 \qquad\qquad 5.\ 30.\ 13$$

$$\Delta_m V = 0 \qquad\qquad 5.\ 30.\ 14$$

The relations (11), (12), (13), (14) have precisely the same form as for the formation of a perfect gaseous mixture from the pure component gases at constant temperature and pressure.

It must be emphasized that this similarity between ideal liquid mixtures and perfect gaseous mixtures as regards dependence of the thermodynamic properties on the composition holds only when the other independent variables are T and P. There are no correspondingly simple relations in terms of the variables T and V, which are moreover an inconvenient set of independent variables for any phase other than a gas.

There is, of course, no similarity between liquid and gaseous mixtures as regards dependence of properties on the pressure. For example, in a perfect gaseous mixture

$$\frac{\partial \mu_i}{\partial P} = V_i = \frac{RT}{P} \qquad\qquad 5.\ 30.\ 15$$

while in a liquid ideal mixture

$$\frac{\partial \mu_i}{\partial P} = \frac{\partial \mu_i^0}{\partial P} = V_i^0 = V_i^\dagger (1 - \varkappa P) \simeq \dot{V}_i^\dagger \qquad 5.\ 30.\ 16$$

where $V_i^\dagger$ denotes the value of V_i^0 as $P \to 0$.

§ 5. 31 RAOULT'S LAW

From formulae (5. 20. 1) and (5. 30. 2) we deduce immediately

$$p_i = x_i\, p_i^0 \qquad\qquad 5.\ 31.\ 1$$

This direct proportionality between partial vapour pressure, or strictly fugacity, and mole fraction is called *Raoult's law*.

For a binary mixture (1) becomes

$$p_1 = (1 - x)p_1^0 \qquad\qquad 5.\ 31.\ 2$$

$$p_2 = xp_2^0 \qquad\qquad 5.\ 31.\ 3$$

$$P = p_1 + p_2 = (1 - x)p_1^0 + xp_2^0 \qquad 5.\ 31.\ 4$$

Thus if the partial vapour pressures, or strictly the fugacities, of the two components of an ideal binary mixture are plotted against the
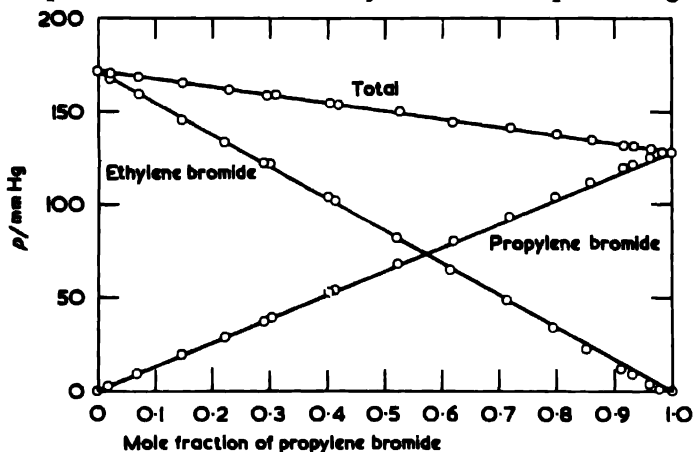
Fig. 5. 4. Partial and total vapour pressures of mixtures of ethylene bromide and propylene bromide at 85 °C.

mole fraction of one of them two straight lines are obtained. The experimental data * for the mixture ethylene bromide and propylene bromide at the temperature 85 °C are shown in fig. 5. 4 and we see
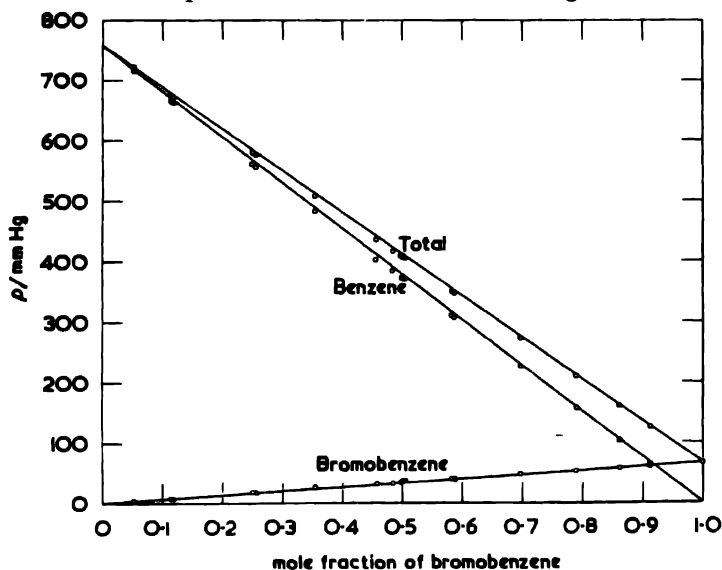
Fig. 5. 5. Partial and total vapour pressures of mixtures of benzene and bromobenzene at 80 °C.

* Von Zawıdzki, Z. phys. Chem. 1900 35 129.

that this mixture is nearly ideal. In fig. 5. 5 we see a similar plot * for the mixture benzene and bromobenzene at 80 °C which is also nearly ideal in spite of the considerable difference between the vapour pressures of the two pure components.

§ 5. 32 OSMOTIC PRESSURE OF IDEAL SOLUTION

To obtain the osmotic pressure of an ideal mixture or ideal solution, regarding the component 1 to which the membrane is permeable as solvent, we have merely to substitute (5. 31. 1) into (5. 27. 10). We thus obtain

$$\frac{\Pi[V_1]}{RT} = -\ln x_1 \qquad 5.\,32.\,1$$

wherein we recall that $[V_1]$ denotes the value of V_1 averaged between the pressures of the two phases in osmotic equilibrium. When we neglect compressibility (1) reduces to

$$\frac{\Pi V_1}{RT} = -\ln x_1 \qquad 5.\,32.\,2$$

§ 5. 33 NON-IDEAL MIXTURES

We have already mentioned that most mixtures are not ideal, but it is convenient to correlate the thermodynamic properties of each real mixture with those of an ideal mixture. This can be achieved formally by two alternative procedures, namely the use of *excess functions* and the use of *activity coefficients*. Both procedures will be described and the relation between the two discussed. For the sake of brevity we shall confine ourselves almost entirely to binary mixtures.

§ 5. 34 MOLAR FUNCTIONS OF MIXING AND EXCESS FUNCTIONS

Consider the process of mixing $1 - x$ moles of species 1 with x moles of species 2, at constant temperature and pressure, so as to form one mole of mixture. The increase of G in this process is called the *molar Gibbs function of mixing* and is denoted by $\Delta_m G$. If the mixture is ideal we have according to (5. 30. 3)

$$\Delta_m G^{\mathrm{I}} = RT\,(1 - x)\ln(1 - x) + RT\,x\ln x \qquad 5.\,34.\,1$$

where the superscript $^{\mathrm{I}}$ denotes ideal. If the mixture is not ideal we denote the excess of $\Delta_m G$ over its ideal value by G_m^{E} and call this the *excess molar Gibbs function*. We have then

* McGlashan and Wingrove, *Trans. Faraday Soc.* 1956 **52** 470.

$$G_m^E = \Delta_m G - \Delta_m G^I = \Delta_m G - RT(1-x)\ln(1-x) - RTx\ln x$$
$$= G_m - (1-x)\mu_1^0 - x\mu_2^0 - RT(1-x)\ln(1-x) - RTx\ln x \qquad 5.34.2$$

We define other molar functions of mixing in a precisely analogous way. For example

$$S_m^E = \Delta_m S - \Delta_m S^I = \Delta_m S + R(1-x)\ln(1-x) + Rx\ln x \quad 5.34.3$$

$$H_m^E = \Delta_m H - \Delta_m H^I = \Delta_m H \qquad 5.34.4$$

$$V_m^E = \Delta_m V - \Delta_m V^I = \Delta_m V \qquad 5.34.5$$

It is clear that the several excess molar functions are interrelated in the same way as the extensive functions from which they are derived. In particular, we have

$$S_m^E = -\frac{\partial G_m^E}{\partial T} \qquad 5.34.6$$

$$V_m^E = \frac{\partial G_m^E}{\partial P} \qquad 5.34.7$$

$$H_m^E = G_m^E - T\frac{\partial G_m^E}{\partial T} \qquad 5.34.8$$

$$U_m^E = G_m^E - T\frac{\partial G_m^E}{\partial T} - P\frac{\partial G_m^E}{\partial P} \qquad 5.34.9$$

We also define excess chemical potentials μ_1^E and μ_2^E of the two component species by

$$\mu_1^E = \Delta_m \mu_1 - \Delta_m \mu_1^I \qquad 5.34.10$$

$$\mu_2^E = \Delta_m \mu_2 - \Delta_m \mu_2^I \qquad 5.34.11$$

from which together with (5.11.15) and (5.11.16) it follows that

$$\mu_1^E = G_m^E - x\frac{\partial G_m^E}{\partial x} \qquad 5.34.12$$

$$\mu_2^E = G_m^E + (1-x)\frac{\partial G_m^E}{\partial x} \qquad 5.34.13$$

The use of excess functions as described here was introduced by Scatchard and Raymond [*].

§ 5.35 EXCESS FUNCTIONS AND VAPOUR PRESSURES

It follows from (5.11.5) (5.19.2) and (5.20.1) that the molar Gibbs function of mixing is related to the partial vapour pressures by

$$\Delta_m G = RT(1-x)\ln\frac{p_1}{p_1^0} + RTx\ln\frac{p_2}{p_2^0} \qquad 5.35.1$$

[*] Scatchard and Raymond, *J. Amer. Chem. Soc.* 1938 **60** 1283.

Combining (1) with (5. 34. 1) and (5. 34. 2) we deduce

$$G_m^E = \Delta_m G - \Delta_m G^I$$

$$= RT (1 - x) \ln \frac{p_1}{p_1^0 (1 - x)} + RTx \ln \frac{p_2}{p_2^0 x} \qquad 5.\,35.\,2$$

As mentioned previously, if the vapour phase may not be regarded as a perfect gas, then each p must be regarded as denoting fugacity. In the present section it will be assumed that deviations of the vapour phase from a perfect gas may be neglected. Under these conditions we can obtain some interesting and simple deductions from (2).

According to the Duhem-Margules relation (5. 21. 5) we have

$$(1 - x) \frac{d \ln p_1}{dx} + x \frac{d \ln p_2}{dx} = 0 \qquad (\text{const. } T) \qquad 5.\,35.\,3$$

Differentiating (2) with respect to x at constant temperature and using (3) we obtain

$$\frac{\partial G_m^E}{\partial x} = RT \ln \frac{p_1^0 \, p_2 \, (1 - x)}{p_2^0 \, p_1 \, x} \qquad 5.\,35.\,4$$

Let us now denote the mole fractions in the vapour phase by $1 - y$ and y to distinguish these from the mole fractions $1 - x$ and x in the liquid. We then have

$$\frac{p_2}{p_1} = \frac{y}{1 - y} \qquad 5.\,35.\,5$$

and using this in (3) we obtain

$$\frac{\partial G_m^E}{\partial x} = RT \ln \frac{p_1^0}{p_2^0} + RT \ln \frac{(1 - x) \, y}{x \, (1 - y)} \qquad 5.\,35.\,6$$

The ratio $(1 - x) \, y / x \, (1 - y)$ is called the *relative volatility* or *volatility ratio* and is denoted by a. We have then

$$\frac{\partial G_m^E}{\partial x} = RT \ln \frac{p_1^0}{p_2^0} + RT \ln a \qquad 5.\,35.\,7$$

Integrating (7) from 0 to x and observing that G_m^E must be zero when $x = 0$ or $x = 1$, we obtain

$$G_m^E (x) = RTx \ln \frac{p_1^0}{p_2^0} + RT \int_0^x \ln a \, dx \qquad 5.\,35.\,8$$

A remarkable feature of (8) is that it enables us to calculate G_m^E from

measurements of the relative volatility a without any measurements of pressure except the vapour pressures p_1^0 and p_2 of the two pure component substances. Furthermore by setting $x = 1$ in (8) and remembering that G_m^E vanishes when $x = 1$ we obtain

$$\int_0^1 \ln a \, dx = \ln \frac{p_2^0}{p_1^0} \qquad\qquad 5.\,35.\,9$$

This relation furnishes a check on the consistency of measurements of a as a function of x. We can illustrate this by using the experimental data on mixtures of water and ethyl alcohol at 25 °C given in table 5.2. In fig. 5.6 $\ln a$ is plotted against x and the straight line is at a distance
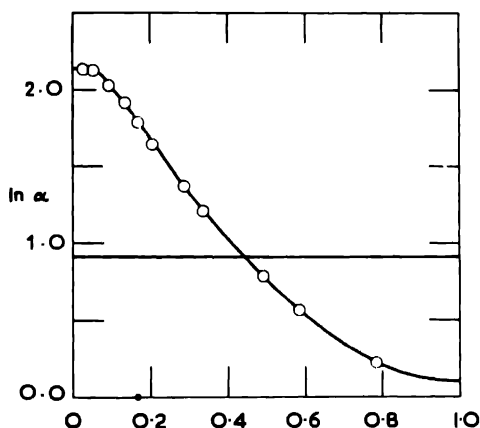
Fig. 5.6. Volatility ratio of mixtures of water and ethyl alcohol at 25 °C.

$\ln (p_2^0/p_1^0)$ from the x axis. The two domains separated by this straight line have equal areas in accordance with formula (9). This valuable procedure for checking experimental consistency was recommended independently and almost simultaneously by Redlich and Kister [*] and by Herington [†]. This kind of plot had previously been recommended by Scatchard and Raymond [‡].

§ 5. 36 ACTIVITY COEFFICIENTS

The excess functions discussed in the preceding sections are the most convenient measures of the departure from ideality of a mixture as a

[*] Redlich and Kister, *Industr. Engng. Chem.* 1948 **40** 345 (paper received 25 November 1946)

[†] Herington, *Nature*, 1947 **160** 610 (letter dated 11 July 1947).

[‡] Scatchard and Raymond, *J. Amer. Chem Soc.* 1938 **60** 1281.

TABLE 5. 2

x	y	α	$\ln \alpha$
0 0252	0.1790	8.421	2.131
0.0523	0.3163	8.387	2.127
0.0916	0.4334	7.582	2.026
0 1343	0.5127	6 782	1.914
0.1670	0.5448	5.969	1.787
0.2022	0.5684	5.197	1.648
0.2848	0 6104	3.935	1 370
0 3368	0.6287	3.334	1.204
0 4902	0.6791	2.201	0.789
0.5820	0 7096	1 755	0.562
0.7811	0 8161	1.244	0.218

whole. When we are more especially concerned with the departure from ideality of the behaviour of a particular component species i, then a more convenient function is the *activity coefficient** f_i defined by

$$a_i = x_i f_i \qquad 5. 36. 1$$

which is equivalent to

$$\frac{\lambda_i}{\lambda_i^0} = \frac{p_i^*}{p_i^{*0}} = x_i f_i \qquad 5. 36. 2$$

It is evident that $f_i \to 1$ as $x_i \to 1$.

The activity coefficient f_i is related to the excess chemical potential μ_i^E by

$$\mu_i^E = RT \ln f_i \qquad 5. 36. 3$$

In the case of a binary mixture we deduce from (3), (5. 34. 12) and (5. 34. 13)

$$RT \ln f_1 = G_m^E - x \frac{\partial G_m^E}{\partial x} \qquad 5. 36. 4$$

$$RT \ln f_2 = G_m^E + (1 - x) \frac{\partial G_m^E}{\partial x} \qquad 5. 36. 5$$

§ 5. 37 RELATION BETWEEN SEVERAL ACTIVITY COEFFICIENTS IN A MIXTURE

When we substitute (5. 36. 2) into the Gibbs-Duhem relation (5. 11. 18) we obtain

$$\Sigma_i x_i \, D \ln x_i + \Sigma_i x_i \, D \ln f_i = 0 \qquad 5. 37. 1$$

But

$$\Sigma_i x_i \, D \ln x_i = \Sigma_i Dx_i = D \Sigma_i x_i = D1 = 0 \qquad 5. 37. 2$$

* The earliest use, that the author has been able to find, of an activity coefficient of a non-electrolyte is by Brönsted, *J. Chem. Soc.* 1921 **119** 574.

and so (1) reduces to

$$\Sigma_i \, x_i \, D \ln f_i = 0 \qquad\qquad 5.\,37.\,3$$

For binary mixtures (3) becomes

$$(1 - x)\frac{\partial \ln f_1}{\partial x} + x\frac{\partial \ln f_2}{\partial x} = 0 \qquad\qquad 5.\,37.\,4$$

§ 5. 38 TEMPERATURE DEPENDENCE OF ACTIVITY COEFFICIENTS

By comparing (5. 36. 2) with (5. 26. 2) we obtain

$$\frac{\partial \ln f_i}{\partial T} = -\frac{H_i - H_i^0}{RT^2} \qquad\qquad 5.\,38.\,1$$

The quantity $H_i - H_i^0$ occurring in (1) is the heat required to b₁ absorbed so as to keep the temperature unchanged when one mole of the pure liquid i is added to a large excess of the mixture. We call this the *partial molar heat of mixing* of the species i.

§ 5. 39 PRESSURE DEPENDENCE OF ACTIVITY COEFFICIENTS

By comparing (5. 36. 2) with (5. 22. 3) we obtain

$$\frac{\partial \ln f_i}{\partial P} = \frac{V_i - V_i^0}{RT} \qquad\qquad 5.\,39.\,1$$

This effect of pressure on activity coefficients is usually negligible.

§ 5. 40 OSMOTIC PRESSURE

Substituting (5. 36. 2) into (5. 27. 8) we obtain for the osmotic pressure with respect to a membrane permeable only to the species 1

$$\frac{\Pi\,[V_1]}{RT} = -\ln\{(1 - x)\,f_1\} \qquad\qquad 5.\,40.\,1$$

The value of f_1 in (1) is that at the pressure P on the pure solvent at osmotic equilibrium.

Alternatively instead of (5. 27. 8) we may use (5. 27. 12) and then obtain

$$\frac{\Pi\,[V_1^0]}{RT} = -\ln\{(1 - x)\,f_1\} \qquad\qquad 5.\,46.\,2$$

where $[V_1^0]$ is the molar volume of the pure solvent at the pressure $P + \frac{1}{2}\Pi$ while f_1 now has the value appropriate to the pressure $P + \Pi$ on the solution at osmotic equilibrium. Usually the difference between corresponding quantities in the two formulae (1) and (2) will be small if not negligible.

§ 5. 41 INTERNAL STABILITY WITH RESPECT TO COMPOSITION

In § 4. 01 and § 4. 02 we discussed the thermal and hydrostatic conditions of internal stability respectively. In a system of a single component these are the only kinds of internal stability to be considered. In a phase of more than one component we have also to consider the condition that the phase should not split into two phases with different compositions.

We can conveniently study this problem for a binary system by reference to a plot of the mean molar Gibbs function G_m against mole fraction x at given T, P. Examples of such a plot are shown in fig. 5. 7
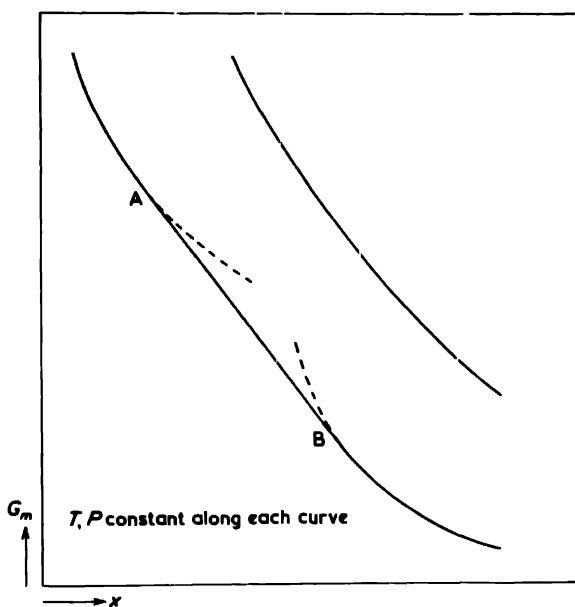
Fig. 5 7. Stable and metastable isotherms.

which in appearance reminds one of fig. 4. 8. If now we imagine a phase of composition x to split into two, one of slightly greater and the other of slightly smaller x, the new value of G_m is then given by a point on the straight line joining the two points representing the two new phases. If this point lies above the one representing the original phase, the system will revert to its original state which is stable. In the contrary case the original phase is unstable. It is then clear from the diagram that while the upper curve represents phases all stable, the phases represented by the dotted portion of the lower curve between

A and B are metastable with respect to a mixture of phases represented by A and B.

Since according to (5. 11. 14)

$$\frac{\partial G_m}{\partial x} = \mu_2 - \mu_1 \qquad\qquad 5.\ 41.\ 1$$

we see that the slope of the curve at any point is equal to $\mu_2 - \mu_1$. Since the two phases A and B are in mutual equilibrium they have equal values of μ_1, μ_2 and consequently of $\mu_2 - \mu_1$ in agreement with the fact that the straight line AB touches the curve at A and B.

§ 5. 42 CRITICAL MIXING

It can happen that at some temperatures the behaviour corresponds to a curve such as the upper one in fig. 5. 7 while at other temperatures, usually lower ones, the behaviour corresponds to a curve such as the lower one. There will then be some temperature at which the change in type of behaviour takes place. This state of affairs is called *critical mixing*. At temperatures on one side of the temperature of critical mixing the two liquids are miscible in all proportions; at temperatures on the other side the miscibility is limited, only phases to the left of A or to the right of B being stable.

We shall now determine the conditions of critical mixing. The lower curve in fig. 5. 7 is concave upwards in the stable regions and in the dotted metastable regions. In these parts of the curve

$$\frac{\partial^2 G_m}{\partial x^2} > 0 \qquad\qquad 5.\ 42.\ 1$$

If we imagine the two dotted curves joined into a single curve then in the middle there must be a part of the curve convex upwards corresponding to completely unstable phases. Hence between A and B there are two points of inflexion C and D where

$$\frac{\partial^2 G_m}{\partial x^2} = 0 \qquad \text{(at C and D)} \qquad\qquad 5.\ 42.\ 2$$

At the temperature of critical mixing these two points merge into a single point at which as well as (2)

$$\frac{\partial^3 G_m}{\partial x^3} = 0 \qquad\qquad 5.\ 42.\ 3$$

Formulae (2) and (3) together express the conditions of critical mixing.

It is convenient to express these conditions of critical mixing (2) and

(3) in terms of the excess molar Gibbs function G_m^E. According to formula (5. 34. 2) we have

$$G_m = G_m^E + (1 - x)\, \mu_1^0 + x\mu_2^0 + RT\, (1 - x)\, \ln\, (1 - x) + RTx \ln x$$

<div align="right">5. 42. 4</div>

By successive differentiation with respect to x we obtain

$$\frac{\partial G_m}{\partial x} = \frac{\partial G_m^E}{\partial x} - \mu_1^0 + \mu_2^0 + RT \ln \frac{x}{1 - x}$$

<div align="right">5. 42. 5</div>

$$\frac{\partial^2 G_m}{\partial x^2} = \frac{\partial^2 G_m^E}{\partial x^2} + \frac{RT}{x\,(1 - x)}$$

<div align="right">5. 42. 6</div>

$$\frac{\partial^3 G_m}{\partial x^3} = \frac{\partial^3 G_m^E}{\partial x^3} + \frac{RT\,(2x - 1)}{x^2\,(1 - x)^2}$$

<div align="right">5. 42. 7</div>

Substituting (6) into (2) and (7) into (3) we obtain the conditions of critical mixing in the form

$$\frac{\partial^2 G_m^E}{\partial x^2} = - \frac{RT}{x\,(1 - x)}$$

<div align="right">5. 42. 8</div>

$$\frac{\partial^3 G_m^E}{\partial x^3} = - \frac{RT\,(2x - 1)}{x^2\,(1 - x)^2}$$

<div align="right">5. 42. 9</div>

The use of these formulae will be illustrated in § 5. 48.

§ 5. 43 EXCESS FUNCTIONS EXPRESSED AS POLYNOMIALS

It is often convenient to express the excess molar Gibbs function G_m^E of a binary mixture as a polynomial in x. We might write such a polynomial as a succession of integral powers of x but such an expression would obscure any symmetry between the two component species. Bearing in mind that G_m^E must vanish identically both when $x_1 = 1 - x = 0$ and when $x_2 = x = 0$, we find it most convenient to write the polynomial in the form *

$$G_m^E = RTx_1x_2 \{A_0 + A_1\,(x_2 - x_1) + A_2\,(x_2 - x_1)^2\}$$
$$= RTx\,(1 - x) \{A_0 + A_1\,(2x - 1) + A_2\,(2x - 1)^2\}$$

<div align="right">5. 43. 1</div>

Higher powers of $x_2 - x_1$ can be included but are seldom required. The coefficients A_0, A_1, A_2 are by definition independent of x but will usually depend on T and maybe also on P.

* Guggenheim, *Trans. Faraday Soc.* 1937 **33** 151 (formula 4. 1).
Redlich and Kister, *Industr. Engng. Chem.* 1948 **40** 345 (formula 8).
Scatchard, *Chem. Rev.* 1949 **44** 9.

From (1) we can as described in § 5. 34 immediately derive formulae for other excess molar functions, in particular

$$H_m^E = -RT^2 x_1 x_2 \left\{ \frac{\partial A_0}{\partial T} + \frac{\partial A_1}{\partial T} (x_2 - x_1) + \frac{\partial A_2}{\partial T} (x_2 - x_1)^2 \right\} \qquad \text{5. 43. 2}$$

$$V_m^E = RT x_1 x_2 \left\{ \frac{\partial A_0}{\partial P} + \frac{\partial A_1}{\partial P} (x_2 - x_1) + \frac{\partial A_2}{\partial P} (x_2 - x_1)^2 \right\} \qquad \text{5. 43. 3}$$

Using (5. 35. 7) we obtain from (1) for the volatility ratio a

$$\ln \frac{p_1^0}{p_2^0} + \ln a = \frac{1}{RT} \frac{\partial G_m^E}{\partial x}$$

$$- -A_0 (x_2 - x_1) + A_1 (6x_1 x_2 - 1) + A_2 (x_2 - x_1) (8x_1 x_2 - 1)$$
$$\text{5. 43. 4}$$

We observe that when $x_1 = x_2 = \frac{1}{2}$ the terms in A_0 and A_2 vanish; when $x_1 x_2 = \frac{1}{6}$ the term in A_1 vanishes and when $x_1 x_2 = \frac{1}{8}$ the term in A_2 vanishes. These points are useful * in determining the best values of A_0, A_1, A_2 to fit experimental values of a.

We can also derive from (1) formulae for the activity coefficients f_1, f_2 by use of (5. 36. 4) and (5. 36. 5). We obtain

$$\ln f_1 = x_2^2 \{A_0 + A_1 (x_2 - 3x_1) + A_2 (x_2 - x_1) (x_2 - 5x_1)\} \qquad \text{5. 43. 5}$$

$$\ln f_2 = x_1^2 \{A_0 - A_1 (x_1 - 3x_2) + A_2 (x_1 - x_2) (x_1 - 5x_2)\} \qquad \text{5. 43. 6}$$

We note that when $x = \frac{1}{8}$ or $\frac{5}{8}$ the terms in A_2 vanish and when $x = \frac{1}{4}$ or $\frac{3}{4}$ the terms in A_1 vanish.

§ 5. 44 SIMPLE MIXTURES AND REGULAR SOLUTIONS

We shall now consider in much greater detail those mixtures for which the coefficients A_1, A_2, as well as those of any higher powers of $x_2 - x_1$, in formula (5. 43. 1) are negligible. For this purpose we shall replace the coefficient RTA_0 by the simpler symbol w. We then have

$$G_m^E = x (1 - x) w \qquad w = w (T, P) \qquad \text{5. 44. 1}$$

where w has the dimensions of a molar energy and is independent of x but will in general depend on T and P. We shall call mixtures having properties defined by (1) *simple mixtures*. Such mixtures are important for several reasons.

In the first place the behaviour of these mixtures is one of the simplest

* Redlich and Kister, *Industr Engng. Chem* 1948 **40** 345.

conceivable after ideal mixtures either from a mathematical or from a physical aspect.

In the second place many binary mixtures show a behaviour which can be represented either accurately or approximately by the formulae of simple mixtures.

In the third place statistical theory predicts that a mixture of two kinds of non-polar molecules of similar simple shape and similar size should obey certain laws to which the formulae of simple mixtures are a useful approximation.

The formulae of simple mixtures, as here defined, were used by Porter * to express empirically partial vapour pressure measurements on mixtures of ethyl ether and acetone at 30 °C and a few measurements at 20 °C. The best value of w at 20 °C was found to be slightly greater than that at 30 °C. Later on Heitler † related these formulae to the model of liquids now usually called the "quasi-crystalline" model and these formulae have been applied to experimental measurements on various mixtures especially by Hildebrand ‡. It was assumed by Heitler † and subsequently generally accepted that the value of w should be independent of temperature although this by no means follows § from the quasi-crystalline model used in the derivation of the formulae.

Meanwhile Hildebrand ** defined a class of mixtures as *regular solutions* when $S^E = 0$. It is doubtful whether a mixture, other than an ideal one, can be accurately regular. Nevertheless the conception of a regular solution, as defined by Hildebrand, can be useful as a basis of comparison for real mixtures. Subsequently Hildebrand used Heitler's formulae with w independent of temperature to represent the properties of many regular solutions. Others came to associate these formulae and the model on which they were based with the name "regular". Hildebrand †† has confirmed his preference that the name "regular" should be restricted to his original definition $S^E = 0$. In conformity with this preference we are introducing the new name *simple mixtures* for mixtures conforming to formula (1) and we emphasize that no restriction is placed on the temperature dependence of w.

* Porter, *Trans Faraday Soc.* 1920 **16** 336.

† Heitler, *Ann. Phys., Lpz.* 1926 **80** 629.

‡ Hildebrand and Scott, *Solubility of Non-electrolytes* 1950.

§ Guggenheim, *Trans. Faraday Soc.* 1948 **44** 1007; *Mixtures* 1952.

** Hildebrand, *Proc. Nat. Acad. Sci. Wash.* 1927 **13** 267; *J. Amer. Chem. Soc.* 1929, **51** 66.

†† Hildebrand, *Nature* 1951 **168** 868.

We shall not in this book concern ourselves further with the detailed properties of mixtures for which $S^E = 0$, that is to say regular solutions as defined by Hildebrand.

§ 5. 45 EXCESS FUNCTIONS OF SIMPLE MIXTURES

We recall the formula (5. 44. 1) which defines simple mixtures

$$G_m^E = x(1-x)w \qquad w = w(T, P) \qquad \text{5. 45. 1}$$

From this we derive, as explained in § 5. 34,

$$S_m^E = -x(1-x)\frac{\partial w}{\partial T} \qquad \text{5. 45. 2}$$

$$H_m^E = x(1-x)\left(w - T\frac{\partial w}{\partial T}\right) \qquad \text{5. 45. 3}$$

$$V_m^E = x(1-x)\frac{\partial w}{\partial P} \qquad \text{5. 45. 4}$$

We shall illustrate the use of these formulae in the following section by considering mixtures of carbon tetrachloride and cyclohexane.

§ 5. 46 PARTIAL VAPOUR PRESSURES OF SIMPLE MIXTURES

From (5. 44. 1) by use of (5. 36. 4) and (5. 36. 5) we deduce for simple mixtures

$$RT \ln f_1 = x^2 w \qquad \text{5. 46. 1}$$

$$RT \ln f_2 = (1-x)^2 w \qquad \text{5. 46. 2}$$

It then follows from other relations in § 5. 36 that

$$\frac{p_1}{p_1^0} = \frac{\lambda_1}{\lambda_1^0} = a_1 = (1-x)f_1 = (1-x)\exp\{x^2 w/RT\} \qquad \text{5. 46. 3}$$

$$\frac{p_2}{p_2^0} = \frac{\lambda_2}{\lambda_2^0} = a_2 = xf_2 = x\exp\{(1-x)^2 w/RT\} \qquad \text{5. 46. 4}$$

For mixtures very dilute with respect to the species 2, when $x \ll 1$, formula (4) approximates to

$$\frac{p_2}{p_2^0} = \frac{\lambda_2}{\lambda_2^0} = a_2 = xf_2 = x\exp(w/RT) \qquad \text{5. 46. 5}$$

This direct proportionality between p_2 and x for small values of x is

called *Henry's law* and it holds not only for simple mixtures but also when higher terms in formula (5. 43. 1) are retained.

We shall now compare the formulae of simple mixtures with the experimental data on mixtures of carbon tetrachloride and cyclohexane. For these mixtures G_m^E has been determined * by vapour pressure measurements at 30, 40, 50, 60 and 70 °C. There are also measurements † of the heat of mixing $\Delta_m H$ at 10, 25, 40 and 55 °C. The experimental values of G_m^E are shown plotted against $x(1-x)$ in fig. 5. 8. According to formula (5. 45. 1) the slopes of the straight lines are the values of w at each temperature. The experimental values of $H_m^E = \Delta_m H$ are shown similarly plotted in fig. 5. 9. According to formula (5. 45. 3) the slopes of the straight lines are the values of $w - T(\partial w/\partial T)$ at each temperature. The fact that the experimental points for $x < \frac{1}{2}$ shown by open symbols and those for $x > \frac{1}{2}$ shown by closed symbols lie on the same straight lines confirms that the laws of simple mixtures are valid within the experimental accuracy. The thermodynamic consistency of the two sets of data requires that both should be fitted by the same values of w and $\partial w/\partial T$. The straight
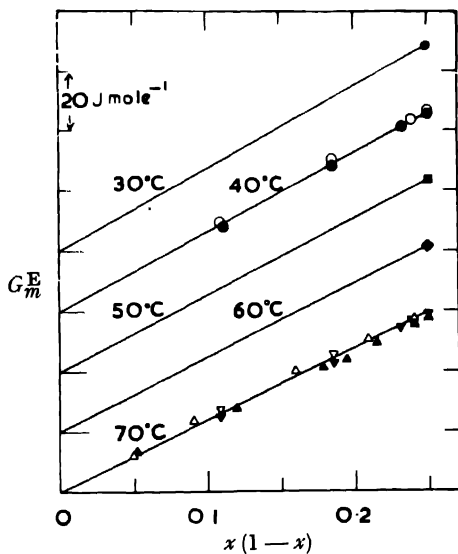
Fig. 5. 8 Excess Gibbs function in mixtures of
carbon tetrachloride and cyclohexane.

* Scatchard, Wood and Mochel, *J. Amer. Chem. Soc.* 1939 **61** 3206.
Brown and Ewald, *Aust. J. Sci. Res.* A 1950 **3** 306.
   † Adcock and McGlashan, *Proc. Roy. Soc.* A 1954 **226** 266.

lines in both fig. 5. 8 and fig. 5. 9 in fact correspond to the single relation *

$$w/\text{J mole}^{-1} = 1176 + 1.96\, T \ln T - 14.18\, T \qquad 5.\,46.\,6$$

so that

$$\left(w - T\,\frac{\partial w}{\partial T}\right)\bigg/\text{J mole}^{-1} = 1176 - 1.96\, T \qquad 5.\,46.\,7$$
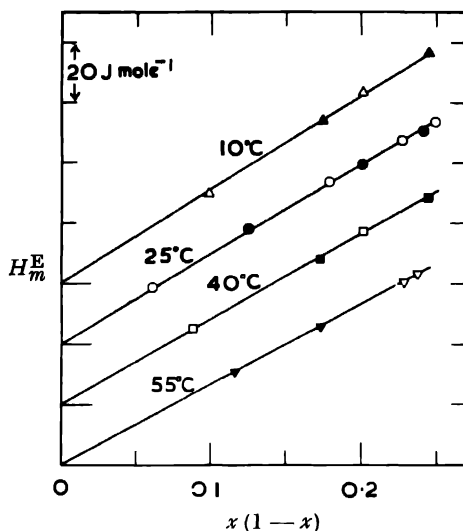
Fig. 5 9. Heat of mixing in mixtures of carbon tetrachloride and cyclohexane.

§ 5. 47 OSMOTIC PRESSURE IN SIMPLE MIXTURES

Substituting from (5. 46. 1) into (5. 40. 1) we obtain for the osmotic pressure with respect to a membrane permeable only to the species 1 n a simple mixture

$$\frac{\Pi\,[V_1]}{RT} = -\ln\,(1-x) - \frac{w}{RT}\,x^2 \qquad 5.\,47.\,1$$

When $x \ll 1$ formula (1) may be approximated by

$$\frac{\Pi\,[V_1]}{RT} = x + \left(\frac{1}{2} - \frac{w}{RT}\right)x^2 \qquad 5.\,47.\,2$$

* Adcock and McGlashan, *Proc. Roy. Soc.* A 1954 **226** 266.

§ 5. 48 CRITICAL MIXING IN SIMPLE MIXTURES

In fig. 5. 10 the quantities $a_1 = p_1/p_1^0$ and $a_2 = p_2/p_2^0$ are plotted against x for $w/RT = 1$ and $w/RT = -2$. When w is positive, the curves lie above the straight lines representing Raoult's law for ideal solutions; this situation is called a *positive deviation* from Raoult's law.

————$w/RT=1$ -----$w/RT=-2$ ————$w/RT=2$
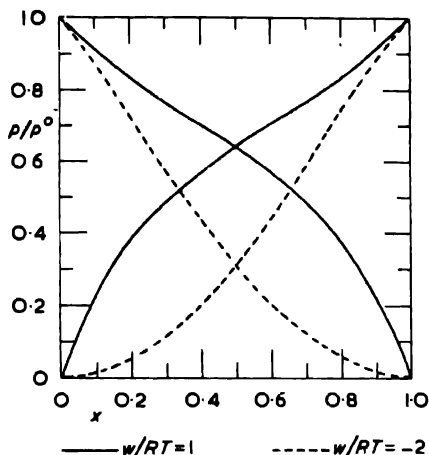
Fig. 5. 10. Partial vapour pressures of simple mixtures: (complete mixing).
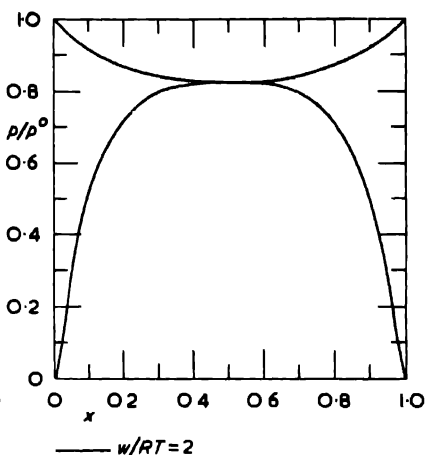
Fig. 5. 11. Partial vapour pressures of simple mixtures: (temperature of critical mixing).

On the other hand when w is negative, both curves lie below the straight line of the ideal solution and this situation is described as a *negative deviation* from Raoult's law.

Fig. 5. 11 gives similar plots for $w/RT = 2$. We shall now show that this is the temperature of critical mixing. We begin by recalling the general conditions for critical mixing (5. 42. 8) and (5. 42. 9)

$$\frac{\partial^2 G_m^E}{\partial x^2} = -\frac{RT}{x(1-x)} \qquad\qquad 5.48.1$$

$$\frac{\partial^3 G_m^E}{\partial x^3} = -\frac{RT(2x-1)}{x^2(1-x)^2} \qquad\qquad 5.48.2$$

We also recall formula (5. 44. 1) which defines simple mixtures

$$G_m^E = x(1-x)w \qquad w = w(T, P) \qquad 5.48.3$$

By successive differentiation of (3) with respect to x we obtain

$$\frac{\partial G_m^E}{\partial x} = (1 - 2x)\, w \qquad\qquad 5.\,48.\,4$$

$$\frac{\partial^2 G_m^E}{\partial x^2} = -2w \qquad\qquad 5.\,48.\,5$$

$$\frac{\partial^3 G_m^E}{\partial x^3} = 0 \qquad\qquad 5.\,48.\,6$$

By substituting (5) into (1) and (6) into (2) we obtain as the conditions for critical mixing in a simple mixture

$$-2w = -\frac{RT}{x\,(1-x)} \qquad\qquad 5.\,48.\,7$$

$$0 = \frac{RT\,(2x-1)}{x^2\,(1-x)^2} \qquad\qquad 5.\,48.\,8$$

From (8) we deduce $x = \frac{1}{2}$, which is incidentally obvious from considerations of symmetry, and substituting this value of x into (7) we obtain for the temperature T_c of critical mixing

$$2RT_c = w \qquad\qquad 5.\,48.\,9$$

in agreement with fig. 5. 11.

When $w/RT > 2$, that is to say at temperatures below that of critical mixing, there is incomplete mixing. A typical example, namely $w/RT = 3$, is shown in fig. 5. 12. If x', x'' denote the compositions of the two phases in mutual equilibrium at a given temperature below that of critical mixing, then x', x'' are determined by the pair of simultaneous equations

$$p_1\,(x') = p_1\,(x'') \qquad\qquad 5.\,48.\,10$$

$$p_2\,(x') = p_2\,(x'') \qquad\qquad 5.\,48.\,11$$

Dividing (10) by p_1^0 and dividing (11) by p_2^0 we obtain the equivalent pair of simultaneous equations

$$a_1\,(x') = a_1\,(x'') \qquad\qquad 5.\,48.\,12$$

$$a_2\,(x') = a_2\,(x'') \qquad\qquad 5.\,48.\,13$$

The conditions (12) and (13) hold for the two phase equilibrium of any binary mixture. In the particular case of simple mixtures we know from (5. 46. 3) and (5. 46. 4) that there is complete symmetry between

a_1 as a function of x and a_2 as a function of $1 - x$. It follows from this symmetry that

$$x' + x'' = 1 \qquad\qquad 5.\,48.\,14$$

and consequently (12) and (13) lead to

$$a_1 (x') = a_1 (x'') = a_2 (1 - x'') = a_2 (x') \qquad\qquad 5.\,48.\,15$$

w/RT=3   ——— stable   ---- unstable
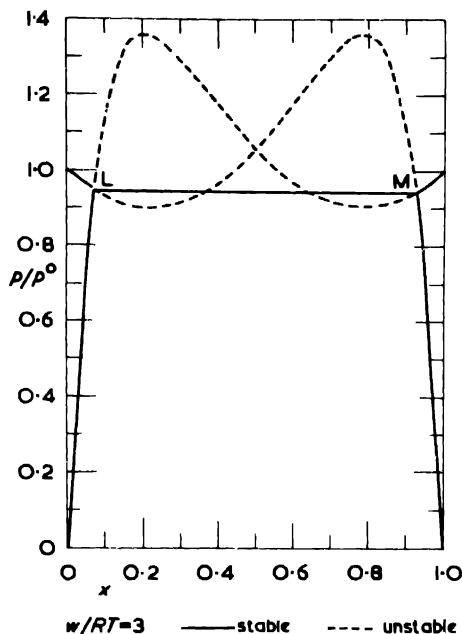
Fig. 5 12   Partial vapour pressures of simple mixtures
(incomplete mixing)

Hence x', x'' are determined by the intersections of the two curves. These are the points L, M in fig. 5. 12. The curves between L and M represent solutions either metastable near L, M or completely unstable towards the middle of the diagram.

When we substitute from (5. 46. 3) and (5. 46. 4) into (15) we obtain as the equation for either x' or x''

$$\frac{1 - x}{x} = \exp \{(1 - 2x)\, w/RT\} \qquad\qquad 5.\,48.\,16$$

If we use the abbreviation $s = 1 - 2x$ we can rewrite (16) as an equation for s in the form

$$s = \tanh (sw/2RT) \qquad\qquad 5.\,48.\,17$$

which can be solved numerically by inspection of tables of the tanh

function. Incidentally we notice from (17) that $s \to 0$ as $w/2RT \to 1$, that is to say at critical mixing.

Pairs of liquids are known, for example water and nicotine, which are completely miscible above a certain critical temperature and below another critical temperature, but are incompletely miscible in the intermediate temperature range. It is interesting to note that even simple mixtures can behave in this way when w is a quadratic function of the temperature provided the three coefficients in the quadratic expression have suitable signs and magnitudes. To be precise if w has the quadratic form *

$$\frac{w}{R} = 2T + \frac{t^2 - (T - T_0)^2}{\Theta} \qquad 5.\ 48.\ 1$$

where Θ, T_0 and t are positive constants and $t < T_0$, then it is clear that $w/R = 2T$ when $T = T_0 - t$ or $T = T_0 + t$. It can also be verified that $w/R > 2T$ when $T_0 - t < T < T_0 + t$ and that $w/R < 2T$ when $T > T_0 + t$ or $T < T_0 - t$. Consequently the temperature range of incomplete miscibility extends from $T_0 - t$ to $T_0 + t$.

Incidentally the converse behaviour would occur, that is complete miscibility only between the two critical temperatures, if Θ were negative. No case of such behaviour is known.

§ 5. 49 EXAMPLE OF UNSYMMETRICAL RELATIONS

One of the characteristic features of simple mixtures, as well as of ideal mixtures, is the notable symmetry between the two component species. This is a direct consequence of the symmetry with respect to x and $1 - x$ in the formula for G_m^E. We shall now briefly illustrate the opposite type of behaviour by a particular hypothetical example.

We return to formula (5. 43. 1). Instead of setting $A_1 = 0$ and $A_2 = 0$ and so obtaining the formulae of simple mixtures, we now set $A_1 = A_0$ and $A_2 = 0$. We then obtain

$$G_m^E = RTAx^2 (1 - x) \qquad 5.\ 49.\ 1$$

where we have written A instead of $2A_0$.

From (2) we obtain, using (5. 36. 4) and (5. 36. 5)

$$\ln f_1 = Ax^2 (2x - 1) \qquad 5.\ 59.\ 2$$

$$\ln f_2 = A2x (1 - x)^2 \qquad 5.\ 49.\ 3$$

A remarkable feature† of this pair of formulae is that, whereas $\ln f_2$

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* Guggenheim, *Faraday Soc. Discussion No.* 15 1953 271.

† I am indebted to Dr M. L. McGlashan for this example of unsymmetrical behaviour.

has for all values of x the same sign as A, the sign of $\ln f_1$ changes at $x = \frac{1}{2}$. This behaviour with $A = \frac{1}{2}$ is illustrated in fig. 5. 13 and fig. 5. 14.
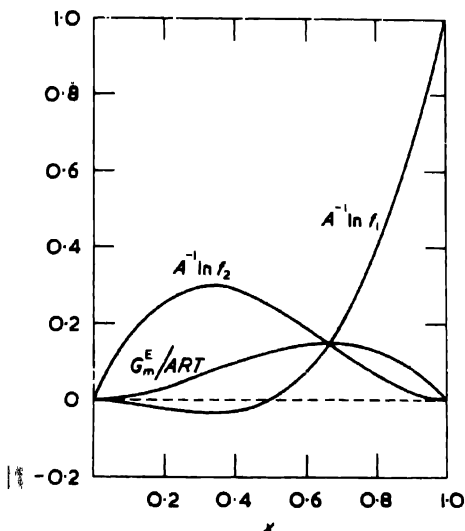
Fig. 5. 13 Example of unsym-metrical excess functions.
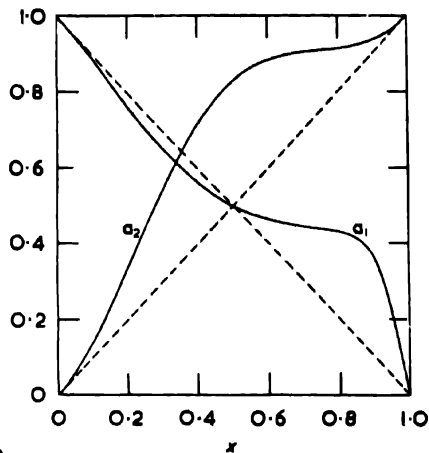
Fig 5. 14. Example of relative activities in a mixture having unsymmetrical excess functions.

§ 5. 50 ATHERMAL MIXTURES OF SMALL AND LARGE MOLECULES

We noticed in § 5. 30 that if two or more species form an ideal mixture, then they mix isothermally without increase or decrease of the heat function. Zero heat of mixing is thus a necessary condition for two or more species to form an ideal mixture, but it is not a sufficient condition. Mixtures, not necessarily ideal, having zero heat of mixing at all compositions are called *athermal mixtures*. Statistical mechanics indicates as a further necessary condition for a mixture to be ideal that the several kinds of molecules should not differ greatly in size. It is accordingly of interest to consider the properties of mixtures of two kinds of molecules sufficiently similar to mix in all proportions without any heat of mixing, but differing widely in size. This is a complicated problem in statistical mechanics which has not been solved completely. It is probable that the shapes of the molecules matter as well as their sizes. However, when we ignore such complications, there are reasons for believing that departures from the laws of ideal mixtures due to wide differences in size between the two species of molecule can be at least semi-quantitatively described by

means of relatively simple formulae in which the only new parameter is the ratio of the molecular volumes.

If ϱ denotes the ratio of the volume of a molecule of type 2 to that of a molecule of type 1, then subject to various restrictions and approximations which we shall not here go into, we may write for the molar Gibbs function of mixing *

$$\Delta_m G = RT (1 - x) \ln \frac{1 - x}{1 - x + \varrho x} + RTx \ln \frac{\varrho x}{1 - x + \varrho x} \qquad 5.\ 50.\ 1$$

Formula (1) is more easily memorized if written in a slightly different form involving the *volume fraction* φ of the second species defined by

$$\varphi = \frac{\varrho x}{1 - x + \varrho x} \qquad 5.\ 50.\ 2$$

Using (2) we can rewrite (1) in the shorter form

$$\Delta_m G = RT (1 - x) \ln (1 - \varphi) + RTx \ln \varphi \qquad 5.\ 50\ 3$$

This simple formula is due to Flory †.

From (3) we deduce using (5. 11. 15), (5. 11. 16) and the formulae of § 5. 19

$$\ln \frac{p_1}{p_1^0} = \ln \frac{\lambda_1}{\lambda_1^0} = \ln a_1 = \ln \frac{1 - x}{1 - x + \varrho x} + \frac{(\varrho - 1)\, x}{1 - x + \varrho x}$$

$$= \ln (1 - \varphi) + \left(1 - \frac{1}{\varrho}\right) \varphi \qquad 5.\ 50.\ 4$$

$$\ln \frac{p_2}{p_2^0} = \ln \frac{\lambda_2}{\lambda_2^0} = \ln a_2 = \ln \frac{\varrho x}{1 - x + \varrho x} - \frac{(\varrho - 1)\,(1 - x)}{1 - x + \varrho x}$$

$$= \ln \varphi - (\varrho - 1)\,(1 - \varphi) \qquad 5.\ 50.\ 5$$

We notice that when $\varrho = 1$ we recover the formulae of ideal mixtures. Of especial interest is the opposite extreme when ϱ is so great that $1/\varrho$ may be neglected compared with unity. Formula (4) then reduces to

$$\ln \frac{p_1}{p_1^0} = \ln \frac{\lambda_1}{\lambda_1^0} = \ln a_1 = \ln (1 - \varphi) + \varphi \qquad (\varrho \to \infty) \qquad 5.\ 50.\ 6$$

We then have the remarkable situation that the lowering of the vapour pressure of the "solvent" species 1 is completely determined by the

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* See Guggenheim, *Mixtures* 1952
† Flory, *J. Chem. Phys.* 1941 **9** 660; 1942 **10** 51

volume fraction of the "solute" species 2. Under these conditions determinations of the vapour pressure of the solvent give no information concerning the size of the solute molecules. These formulae are relevant to solutions of rubber or polystyrene in certain non-polar solvents such as benzene and toluene.

§ 5. 51 OSMOTIC PRESSURE IN ATHERMAL MIXTURES

By substituting (5. 50. 4) into (5. 27. 9) we obtain for the osmotic pressure with respect to a membrane permeable only to the species 1 with small molecules

$$\frac{\Pi[V_1]}{RT} = -\ln(1-\varphi) - \left(1 - \frac{1}{\varrho}\right)\varphi \qquad 5.\ 51.\ 1$$

If we expand $\ln(1-\varphi)$ in powers of φ we obtain

$$\frac{\Pi[V_1]}{RT} = \frac{\varphi}{\varrho} + \frac{1}{2}\varphi^2 + \frac{1}{3}\varphi^3 + \ldots \qquad 5.\ 51.\ 2$$

From (2) and (5. 50. 2) we see that in the limit of infinite dilution $\Pi \propto x$ as usual, but for this state of affairs it is not sufficient that $\varphi \ll 1$, the much more stringent condition $\varrho\varphi \ll 1$ being required. If we merely assume that $\varphi \ll 1$ formula (2) reduces to

$$\frac{\Pi[V_1]}{RT} = \frac{\varphi}{\varrho} + \frac{1}{2}\varphi^2 \qquad (\varphi \ll 1) \qquad 5.\ 51.\ 3$$

and the term $\frac{1}{2}\varphi^2$ will swamp the term φ/ϱ unless $\varphi < \varrho^{-1}$. It follows from this that in a solution of macromolecules measurements of osmotic pressure cannot yield simple or reliable information concerning the size of the solute macromolecules unless the solutions are so dilute that $\varphi \ll \varrho^{-1}$ which implies that $x \ll \varrho^{-2}$.

§ 5. 52 INTERFACIAL LAYERS

We shall now consider the thermodynamics of interfacial layers between two bulk phases each containing the same two components There are two cases to distinguish: first an interface between a liquid mixture and its vapour, when the interfacial tension is called the *surface tension*; second an interface between two liquid layers containing in different proportions two incompletely miscible components.

We shall first discuss the liquid-vapour interface using an approximation sufficient for most if not all practical applications. We shall next give a similar approximate treatment of a liquid-liquid interface. Finally we shall give an accurate treatment applicable in principle to either type of interface, but of small practical use.

§ 5. 53 LIQUID-VAPOUR INTERFACE

We begin with formula (1. 55. 3) applied to a system of two components 1 and 2. Thus

$$-\mathrm{d}\gamma = S^\sigma\,\mathrm{d}T - \tau\mathrm{d}P + \Gamma_1\,\mathrm{d}\mu_1 + \Gamma_2\,\mathrm{d}\mu_2 \qquad 5.\,53.\,1$$

where we have dropped the subscript u in S_u^σ which we used in § 1. 55 to denote entropy per unit area of the interfacial layer. At the same time in the liquid phase we have according to (5. 11. 12) and (5. 11. 13)

$$\mathrm{d}\mu_1 = -S_1\,\mathrm{d}T + V_1\,\mathrm{d}P + \frac{\partial\mu_1}{\partial x}\,\mathrm{d}x \qquad 5.\,53.\,2$$

$$\mathrm{d}\mu_2 = -S_2\,\mathrm{d}T + V_2\,\mathrm{d}P + \frac{\partial\mu_2}{\partial x}\,\mathrm{d}x \qquad 5.\,53.\,3$$

where we have omitted superscripts from quantities relating to the liquid phase.

In our initial treatment of a liquid-vapour interface we shall make approximations similar to those used in § 4. 72 for a single component interface.

In the first place we assume that PV_1 and PV_2 are in the liquid phase so small compared with RT that they may be neglected.

In the second place we assume that the two geometrical surfaces separating the interfacial phase from the two bulk phases are placed so near to each other that terms in $P\tau$ may also be neglected. We accordingly replace (1), (2), (3) by

$$-\mathrm{d}\gamma = S^\sigma\,\mathrm{d}T + \Gamma_1\,\mathrm{d}\mu_1 + \Gamma_2\,\mathrm{d}\mu_2 \qquad 5.\,53.\,4$$

$$\mathrm{d}\mu_1 = -S_1\,\mathrm{d}T + \frac{\partial\mu_1}{\partial x}\,\mathrm{d}x \qquad 5.\,53.\,5$$

$$\mathrm{d}\mu_2 = -S_2\,\mathrm{d}T + \frac{\partial\mu_2}{\partial x}\,\mathrm{d}x \qquad 5.\,53.\,6$$

Substituting (5) and (6) into (4) we obtain

$$-\mathrm{d}\gamma = (S^\sigma - \Gamma_1 S_1 - \Gamma_2 S_2)\,\mathrm{d}T + \left(\Gamma_1\frac{\partial\mu_1}{\partial x} + \Gamma_2\frac{\partial\mu_2}{\partial x}\right)\mathrm{d}x \qquad 5.\,53.\,7$$

The system of two components in liquid and vapour has two degrees of freedom. There are consequently two independent variables, for which we choose T and x. Formula (7) thus expresses variations of the surface tension γ in terms of variations dT and dx of the two independent variables.

Since the quantities $\partial\mu_1/\partial x$ and $\partial\mu_2/\partial x$ on the right of (7) are related by the Gibbs-Duhem relation (5. 11. 19)

$$(1 - x)\,\frac{\partial\mu_1}{\partial x} + x\,\frac{\partial\mu_2}{\partial x} = 0 \qquad\qquad 5.\,53.\,8$$

we can use this relation to eliminate either of them. If for example we eliminate $\partial\mu_1/\partial x$ we obtain

$$- \, d\gamma = (S^\sigma - \Gamma_1 S_1 - \Gamma_2 S_2)\,dT + \left(\Gamma_2 - \frac{x\Gamma_1}{1-x}\right)\frac{\partial\mu_2}{\partial x}\,dx \qquad 5.\,53.\,9$$

By this elimination we have unavoidably destroyed the symmetry between the components 1 and 2.

§ 5. 54 INVARIANCE OF RELATIONS

We recall that according to the definition in § 1. 51 of a surface phase the properties associated with it depend on the positions of the boundaries AA' and BB' in fig. 1. 2. As in § 4. 71 we shall henceforth refer to the boundary between surface layer and liquid as Lσ and that between surface layer and gas as Gσ. Since the precise positions assigned to these geometrical boundaries are partly arbitrary, the values assigned to such quantities as Γ_1, Γ_2, S^σ are also arbitrary. We can nevertheless verify that our formulae are invariant with respect to shifts of either or both of these boundaries. It is hardly necessary to mention that the intensive variables T, μ_1, μ_2 are unaffected by shifts of either boundary. It is also clear from the definition of γ in § 1. 52 that its value is invariant.

Let us now consider a shift of the plane boundary Lσ a distance $\delta\tau$ away from the gas phase. Then Γ_1 becomes increased by the number of moles of the species 1 in a cylinder of liquid of height $\delta\tau$, of cross-section unity and so of volume $\delta\tau$. But the total number of moles in the volume $\delta\tau$ is $\delta\tau/V_m$ of which the number of species 1 is $(1-x)\delta\tau/V_m$. Similarly Γ_2 becomes increased by $x\delta\tau/V_m$. Consequently although shifting the boundary Lσ alters the values of Γ_1 and Γ_2, the quantity

$$\Gamma_2 - \frac{x\Gamma_1}{1-x} \qquad\qquad 5.\,54.\,1$$

remains unchanged. The invariant quantity (1) is essentially the same as a quantity defined by Gibbs in a more abstract manner and denoted by him by the symbol $\Gamma_{2(1)}$.

Similarly when the boundary Lσ is shifted a distance $\delta\tau$ away from the gas phase, S^σ becomes increased by the entropy contained in a cylinder of liquid of volume $\delta\tau$, that is to say by an amount

$$S_m \, \delta\tau/V_m = \{(1 - x) \, S_1 + xS_2\} \, \delta\tau/V_m$$

At the same time $\Gamma_1 S_1$ is increased by $S_1 (1 - x) \, \delta\tau/V_m$ and $\Gamma_2 S_2$ by $S_2 x\delta\tau/V_m$. Consequently the quantity

$$S^\sigma - \Gamma_1 S_1 - \Gamma_2 S_2 \qquad\qquad 5.\,54.\,2$$

occurring in (5. 53. 9) remains invariant.

With regard to a shift of the geometrical surface Gσ, little need be said in the present connection. For our approximation of neglecting terms in $P\tau$, as we are doing, is equivalent to assuming that the quantity of matter per unit volume in the gas phase is negligible compared with that in unit volume of the surface layer. Consequently if we shifted the geometrical surface Gσ away from the liquid even to the extent of doubling the value of τ, the change in the physical content of the surface layer would be negligible and consequently the values of Γ_1, Γ_2, S^σ would not be appreciably affected.

§ 5. 55 TEMPERATURE COEFFICIENT OF SURFACE TENSION

If we apply formula (5. 53. 9) to variations of temperature at constant composition x of the liquid we obtain

$$-\frac{d\gamma}{dT} = S^\sigma - \Gamma_1 S_1 - \Gamma_2 S_2 \qquad \text{(const. } x) \qquad 5.\,55.\,1$$

This relation involving entropies can be transformed to one involving energies as follows. Since we are neglecting terms in PV_1 and PV_2 we may replace (5. 11. 3) by the approximation

$$\mu_1 = F_1 = U_1 - TS_1 \qquad\qquad 5.\,55.\,2$$

and similarly

$$\mu_2 = F_2 = U_2 - TS_2 \qquad\qquad 5.\,55.\,3$$

Applying formula (1. 54. 6) to unit area and neglecting the term containing $V^\sigma = \tau A$, we have

$$\Gamma_1 \mu_1 + \Gamma_2 \mu_2 = F^\sigma - \gamma = U^\sigma - TS^\sigma - \gamma \qquad 5.\,55.\,4$$

We now use (2), (3), (4) to eliminate S^σ, S_1, S_2 from (1). We thus obtain

$$\gamma - T\frac{d\gamma}{dT} = U^\sigma - \Gamma_1 U_1 - \Gamma_2 U_2 \qquad 5.\,55.\,5$$

It is worth noticing that the right side of (1) is the entropy of unit area of interface less the entropy of the same material content in the liquid phase. Likewise the right side of (5) is the energy of unit area of interface less the energy of the same material content in the liquid ' ise. More pictorially we may say that it is the energy which must be supplied to prevent any change of temperature when unit area of surface is formed from the liquid. It is sometimes called the *surface energy* per unit area, but this name belongs more properly to U^σ.

§ 5. 56 VARIATIONS OF COMPOSITION

If we apply (5. 53. 7) to a variation of composition at constant temperature we obtain, using (5. 20. 2)

$$-\frac{\partial \gamma}{\partial x} = \Gamma_1 \frac{\partial \mu_1}{\partial x} + \Gamma_2 \frac{\partial \mu_2}{\partial x}$$

$$= RT\left(\Gamma_1 \frac{\partial \ln \lambda_1}{\partial x} + \Gamma_2 \frac{\partial \ln \lambda_2}{\partial x}\right)$$

$$= RT\left(\Gamma_1 \frac{\partial \ln a_1}{\partial x} + \Gamma_2 \frac{\partial \ln a_2}{\partial x}\right)$$

$$= RT\left(\Gamma_1 \frac{\partial \ln p_1}{\partial x} + \Gamma_2 \frac{\partial \ln p_2}{\partial x}\right) \qquad \text{(const. } T\text{)} \quad 5.\,56.\,1$$

When we combine (1) with the Gibbs-Duhem relation (5. 11. 20) or with the Duhem-Margules relation (5. 21. 5) we obtain

$$-\frac{1}{RT}\frac{\partial \gamma}{\partial x} = -\left\{(1-x)\,\Gamma_2 - x\Gamma_1\right\}\frac{1}{x}\frac{\partial \ln \lambda_1}{\partial x}$$

$$= \left\{(1-x)\,\Gamma_2 - x\Gamma_1\right\}\frac{1}{1-x}\frac{\partial \ln \lambda_2}{\partial x} \qquad 5.\,56.\,2$$

or alternatively

$$-\frac{1}{RT}\frac{\partial \gamma}{\partial x} = -\left\{(1-x)\,\Gamma_2 - x\Gamma_1\right\}\frac{1}{x}\frac{\partial \ln p_1}{\partial x}$$

$$= \left\{(1-x)\,\Gamma_2 - x\Gamma_1\right\}\frac{1}{1-x}\frac{\partial \ln p_2}{\partial x} \qquad 5.\,56.\,3$$

From (3) we see that from measurements of γ and p_1 or p_2 over a range of compositions we can for each composition compute the value of the quantity I defined by

$$I = (1 - x)\, \Gamma_2 - x\Gamma_1 \qquad\qquad 5.\,56.\,4$$

We have already verified in § 5. 54 that $I/(1 - x)$ is invariant with respect to shift in position of the boundary $L\sigma$ between the liquid and the interface. Obviously the same holds for I itself. Values can be assigned to Γ_1 and Γ_2 individually only by adopting some more or less arbitrary convention *. We shall illustrate this by a numerical example in the next section. Since Γ_1, Γ_2 must be finite, it follows from (4) that

$$\Gamma_2/I \to 1 \quad \text{as} \quad x \to 0 \qquad\qquad 5.\,56.\,5$$

$$- \Gamma_1/I \to 1 \quad \text{as} \quad x \to 1 \qquad\qquad 5.\,56.\,6$$

This implies that for small values of x the value of Γ_2 is unaffected by the position assigned to the boundary $L\sigma$ and that for small values of $1 - x$ the value of Γ_1 is unaffected. Consequently when $x \ll 1$ we may regard I as a measure of the positive adsorption Γ_2 of species 2 at the surface and when $1 - x \ll 1$ we may regard I as a measure of the negative adsorption $- \Gamma_1$ of the species 1. At intermediate values of x no such simple physical meaning can be attached to I. We may however regard I as a measure of relative adsorption of the two species.

In the special case of an ideal mixture formula (3) becomes

$$- \frac{1}{RT} \frac{\partial \gamma}{\partial x} = \frac{\Gamma_2}{x} - \frac{\Gamma_1}{1 - x} = \frac{I}{x\,(1 - x)} \qquad\qquad 5.\,56.\,7$$

§ 5. 57 EXAMPLE OF WATER AND ALCOHOL

We shall now consider the experimental data for mixtures of water and alcohol in order to illustrate the use of the formulae of the preceding section. The experimental data for the partial vapour pressures have already been given in fig. 5. 2 and table 5. 1 where we verified that they are consistent with the Duhem-Margules relation. In table 5. 3 the first three columns repeat those of table 5. 1, the subscripts $_1$ denoting water and $_2$ alcohol. The fourth column gives experimental values of the surface tension γ. The fifth column gives values of

* Guggenheim and Adam, *Proc. Roy. Soc.* A 1933 **139** 231.

TABLE 5. 3

Mixtures of water and ethyl alcohol at 25 °C

Determination of $I = (1-x)\,\Gamma_2 - x\Gamma_1$

x	p_1 mm Hg	p_2 mm Hg	γ erg cm^{-2}	$-\partial\gamma/\partial\ln p_2$ erg cm^{-2}	$10^{10}I$ mole cm^{-2}	10^2I molecules Å^{-2}
0	23.75	0.0	72.2	0 0	0 0	0 0
0.1	21.7	17 8	36 4	15 6	5 6	9.3
0 2	20.4	26.8	29 7	16.0	5.1	8 5
0 3	19.4	31.2	27 6	14 6	4.1	6 8
0 4	18.35	34.2	26 35	12 6	3.0	5.0
0.5	17.3	36 9	25 4	10 5	2.1	3.5
0 6	15.8	40.1	24 6	8.45	1.4	2.3
0 7	13.3	43.9	23 85	7 15	0 8	1.3
0 8	10 0	48.3	23 2	6 2	0 5	0.8
0 9	5.5	53.3	22 6	5 45	0 2	0 3
1 0	0.0	59.0	22.0	5 2	0.0	0 0

$-\partial\gamma/\partial\ln p_2$ obtained by plotting γ against $\ln p$ and measuring slopes. The sixth column gives values of

$$I = (1-x)\,\Gamma_2 - x\Gamma_1 \qquad\qquad 5.\,57.\,1$$

calculated from (5. 56. 3) which can be rewritten in the form

$$-\frac{\partial\gamma}{\partial\ln p_2} = \frac{RTI}{1-x} \qquad\qquad 5.\,57.\,2$$

The values of I are given in the sixth column in moles cm^{-2}. In the seventh column the corresponding molecular quantity is given in molecules Å^{-2}.

As we have repeatedly emphasized, this is as far as one can go without using some non-thermodynamic convention. We shall now give an example of such a convention. Let us assume that the inter-facial layer is unimolecular and that each molecule of water occupies a constant area of interface and likewise each molecule of alcohol. This assumption may be expressed by

$$A_1\Gamma_1 + A_2\Gamma_2 = 1 \qquad (A_1,\,A_2\ \text{const.}) \qquad 5.\,57.\,3$$

We may call A_1, A_2 the *partial areas* of the two species in the interface. The essence of our assumption is not the definition of these quantities, but the assignment to them of definite constant values which can neither be determined nor be verified by thermodynamic means.

As an example we might assume

$$A_1 = 0.04 \times 10^{10} \text{ cm}^2 \text{ mole}^{-1}$$

$$A_2 = 0.12 \times 10^{10} \text{ cm}^2 \text{ mole}^{-1}$$

5. 57. 4

corresponding to molecular cross-sections

$$A_1/L = 7 \text{ Å}^2$$

$$A_2/L = 20 \text{ Å}^2$$

5. 57. 5

The relation (3) with the values of A_1, A_2 given by (4) is sufficient to determine values of Γ_1, Γ_2 from the values of the expression (1) already given in table 5. 3. The results of the calculation are given in table 5. 4.

TABLE 5. 4

Mixtures of water and ethyl alcohol at 25 °C
Values of Γ_1 and Γ_2 calculated from

$$A_1\Gamma_1 + A_2\Gamma_2 = 1$$

with A_1 0 04 $\times$ 10^{10} cm² mole⁻¹ of water
$A_2 = 0 12 \times 10^{10}$ cm² mole⁻¹ of alcohol

x	$\dfrac{10^{10}I}{\text{mole cm}^{-2}}$	$\dfrac{10^{10}\,\Gamma_2}{\text{mole cm}^{-2}}$	$\dfrac{10^{10}\,\Gamma_1}{\text{mole cm}^{-2}}$	$\dfrac{\Gamma_2}{\Gamma_1 + \Gamma_2}$
0 0	0 0	0 0	25 0	0.00
0.1	5.6	6 8	4 6	0.60
0.2	5 1	7.25	3 25	0.69
0.3	4.1	7.25	3 25	0 69
0.4	3 0	7.25	3 25	0 69
0.5	2.1	7.3	3.1	0.70
0.6	1.4	7.45	2.65	0.74
0.7	0.8	7 65	2.0	0.79
0.8	0.5	7 9	1.3	0 86
0.9	0.2	8.1	0 7	0.94
1.0	0.0	8.35	0.0	1 00

The first column gives the mole fraction x of alcohol, the second the values of I taken from the previous table, the third and fourth columns the values of Γ_1, Γ_2 calculated by means of (3). The fifth column gives values of $\Gamma_2/(\Gamma_1 + \Gamma_2)$ which we may call the *mole fraction* of alcohol in the surface layer. As the mole fraction thus calculated, in the surface layer increases steadily with the mole fraction in the liquid, we may conclude that although the model on which the assumptions (3), (4), (5) were based is admittedly arbitrary, at least it does not lead to unreasonable or surprising results.

§ 5. 58 INTERFACE BETWEEN TWO BINARY LIQUIDS

We turn now to consider the interface between two liquid phases of two components. Two such phases may or may not be simple, but they obviously cannot be ideal. In our initial treatment we shall make approximations similar to those in § 5. 53.

We assume that in a liquid phase PV_1 and PV_2 are so small compared with RT that they may be neglected. This assumption now applies to both liquid phases. Just as in § 5. 53 we also neglect terms in $P\tau$.

There is an important physical difference between the significance of our approximate treatment of a liquid-vapour interface in the previous sections and the approximate treatment we are now about to give of a liquid-liquid interface. In the case of the liquid-vapour system we took as independent variables the temperature and composition of the liquid phase. Since the system has two degrees of freedom, these determine the composition and pressure of the vapour phase. Moreover the consequent variations of pressure are significant in determining the thermodynamic properties of the vapour phase. In our present discussion of a liquid-liquid system we are assuming that the thermodynamic properties of all phases, that is both liquids and interface, are independent of the pressure. We are thus effectively suppressing variability of pressure as a possible degree of freedom. But when we do this, a single liquid binary phase has only two remaining degrees of freedom, so that we might take as variables either T, x which are independent or T, μ_1, μ_2 subject to the Gibbs-Duhem relation. Correspondingly in a system of two binary liquid phases the variables T, μ_1, μ_2 are subject to two Gibbs-Duhem relations, one in each phase. Thus the system has effectively only one degree of freedom instead of two. Hence the temperature completely determines the composition of both liquid phases and so also the properties of the interface.

We may alternatively describe the situation as follows. A binary liquid-liquid system, like a binary liquid-vapour system has two degrees of freedom. We may therefore take as independent variables T, P and these will then determine the composition of both phases and so also the properties of the interface. When however we use the approximation of treating the properties of every phase as effectively independent of P, then clearly all the equilibrium properties are completely determined by T.

We accordingly proceed to determine how the interfacial tension depends on the temperature.

§ 5. 59 TEMPERATURE DEPENDENCE OF INTERFACIAL TENSION

We begin with formula (5. 53. 4)

$$-d\gamma = S^\sigma \, dT + \Gamma_1 \, d\mu_1 + \Gamma_2 \, d\mu_2 \qquad 5.\,59.\,1$$

which applies as well to a liquid-liquid as to a liquid-vapour interface. We also have a Gibbs-Duhem relation in each of the liquid phases. It is convenient to use these in the form (1. 38. 3) with the term $V_m \, dP$ neglected. We have accordingly, denoting the two liquid phases by the superscripts α and β,

$$S_m^\alpha \, dT + (1 - x^\alpha) \, d\mu_1 + x^\alpha \, d\mu_2 = 0 \qquad 5.\,59.\,2$$

$$S_m^\beta \, dT + (1 - x^\beta) \, d\mu_1 + x^\beta \, d\mu_2 = 0 \qquad 5.\,59.\,3$$

wherein we have omitted the superscripts on T, μ_1, μ_2 since these have the same values throughout the system. We recall that S_m^α, S_m^β denote the mean molar entropies in the two phases.

To obtain the dependence of γ on the temperature, we have merely to eliminate $d\mu_1$, $d\mu_2$ from (1), (2), (3). We thus obtain

$$-\frac{d\gamma}{dT} = \frac{\begin{vmatrix} S^\sigma & S_m^\alpha & S_m^\beta \\ \Gamma_1 & 1 - x^\alpha & 1 - x^\beta \\ \Gamma_2 & x^\alpha & x^\beta \end{vmatrix}}{x^\beta - x^\alpha} = \frac{\begin{vmatrix} S^\sigma & S_m^\alpha & S_m^\beta \\ \Gamma_1 + \Gamma_2 & 1 & 1 \\ \Gamma_2 & x^\alpha & x^\beta \end{vmatrix}}{x^\beta - x^\alpha} \qquad 5.\,59.\,4$$

There seems to be no alternative simpler formula having as high an accuracy.

§ 5. 60 ACCURATE FORMULAE

For the sake of completeness we shall now derive formulae, in principle applicable to any interface in a system of two components, in which we do not neglect the terms in $V dP$ or τdP. We however warn the reader that these formulae are too complicated to be of any practical use.

We accordingly revert to formula (5. 53. 1), namely

$$- d\gamma = S^\sigma \, dT - \tau dP + \Gamma_1 \, d\mu_1 + \Gamma_2 \, d\mu_2 \qquad 5.\,60.\,1$$

and formulae (5. 53. 2) and (5. 53. 3) applied to each of the two phases α, β

$$d\mu_1^\alpha = - S_1^\alpha \, dT + V_1^\alpha \, dP + \frac{\partial \mu_1^\alpha}{\partial x^\alpha} \, dx^\alpha \qquad 5.\,60.\,2$$

$$\mathrm{d}\mu_2^a = - S_2^a\, \mathrm{d}T + V_2^a\, \mathrm{d}P + \frac{\partial \mu_2^a}{\partial x^a}\, \mathrm{d}x^a \qquad 5.\,60.\,3$$

$$\mathrm{d}\mu_1^\beta = - S_1^\beta\, \mathrm{d}T + V_1^\beta\, \mathrm{d}P + \frac{\partial \mu_1^\beta}{\partial x^\beta}\, \mathrm{d}x^\beta \qquad 5.\,60.\,4$$

$$\mathrm{d}\mu_2^\beta = - S_2^\beta\, \mathrm{d}T + V_2^\beta\, \mathrm{d}P + \frac{\partial \mu_2^\beta}{\partial x^\beta}\, \mathrm{d}x^\beta \qquad 5.\,60.\,5$$

We shall also use the Gibbs-Duhem relation in the form (5. 11. 19) in both the phases a, β

$$(1 - x^a)\, \frac{\partial \mu_1^a}{\partial x^a} + x^a\, \frac{\partial \mu_2^a}{\partial x^a} = 0 \qquad 5.\,60.\,6$$

$$(1 - x^\beta)\, \frac{\partial \mu_1^\beta}{\partial x^\beta} + x^\beta\, \frac{\partial \mu_2^\beta}{\partial x^\beta} = 0 \qquad 5.\,60.\,7$$

For any variations maintaining equilibrium, we have as usual

$$\mathrm{d}\mu_1^a = \mathrm{d}\mu_1^\beta = \mathrm{d}\mu_1 \qquad 5.\,60.\,8$$

$$\mathrm{d}\mu_2^a = \mathrm{d}\mu_2^\beta = \mathrm{d}\mu_2 \qquad 5.\,60.\,9$$

If we multiply (8) by $(1 - x^\beta)$, (9) by x^β, substitute from (2), (3), (4), (5) and add, we obtain using (7)

$$\begin{aligned}
0 = &- \{ (1 - x^\beta)\, (S_1^a - S_1^\beta) + x^\beta\, (S_2^a - S_2^\beta) \}\, \mathrm{d}T \\
&+ \{ (1 - x^\beta)\, (V_1^a - V_1^\beta) + x^\beta\, (V_2^a - V_2^\beta) \}\, \mathrm{d}P \\
&+ \left\{ (1 - x^\beta)\, \frac{\partial \mu_1}{\partial x^a} + x^\beta\, \frac{\partial \mu_2}{\partial x^a} \right\}\, \mathrm{d}x^a
\end{aligned} \qquad 5.\,60.\,10$$

If further we substitute (2), (3) into (1) we obtain

$$- \mathrm{d}\gamma = (S^\sigma - \Gamma_1 S_1^a - \Gamma_2 S_2^a)\, \mathrm{d}T - (\tau - \Gamma_1 V_1^a - \Gamma_2 V_2^a)\, \mathrm{d}P$$

$$+ \left\{ \Gamma_1\, \frac{\partial \mu_1}{\partial x^a} + \Gamma_2\, \frac{\partial \mu_2}{\partial x^a} \right\}\, \mathrm{d}x^a \qquad 5.\,60.\,11$$

If we now eliminate $\mathrm{d}P$ between (10) and (11) we obtain

$$- \mathrm{d}\gamma = \left(\Delta_{a\sigma}S - \frac{\Delta_{a\sigma}V\, \Delta_{a\beta}S}{\Delta_{a\beta}V} \right)\, \mathrm{d}T$$

$$+ \left(\Gamma_1 + \frac{\Delta_{a\sigma}V\, (1 - x^\beta)}{\Delta_{a\beta}V} \right)\, \frac{\partial \mu_1}{\partial x^a}\, \mathrm{d}x^a$$

$$+ \left(\Gamma_2 + \frac{\Delta_{a\sigma}V\, x^\beta}{\Delta_{a\beta}V} \right)\, \frac{\partial \mu_2}{\partial x^a}\, \mathrm{d}x^a \qquad 5.\,60.\,12$$

where we have used the following abbreviations

$$\Delta_{\alpha\beta}S = (1 - x^\beta) (S_1^\beta - S_1^\alpha) + x^\beta (S_2^\beta - S_2^\alpha) \qquad 5.\ 60.\ 13$$

$$\Delta_{\alpha\beta}V = (1 - x^\beta) (V_1^\beta - V_1^\alpha) + x^\beta (V_2^\beta - V_2^\alpha) \qquad 5.\ 60.\ 14$$

$$\Delta_{\alpha\sigma}S = S^\sigma - \Gamma_1 S_1^\alpha - \Gamma_2 S_2^\alpha \qquad 5.\ 60.\ 15$$

$$\Delta_{\alpha\sigma}V = \tau - \Gamma_1 V_1^\alpha - \Gamma_2 V_2^\alpha \qquad 5.\ 60.\ 16$$

From these definitions we observe that $\Delta_{\alpha\beta}S$ is the entropy increase and $\Delta_{\alpha\beta}V$ the volume increase when one mole of the phase β is formed at constant temperature and constant pressure by taking the required amounts of the two components from the phase α. Likewise $\Delta_{\alpha\sigma}S$ is the entropy increase and $\Delta_{\alpha\sigma}V$ the volume increase when unit area of the surface layer σ is formed at constant temperature and constant pressure by taking the required amounts of the two components from the phase α.

Finally we can eliminate $\partial\mu_1/\partial x^\alpha$ (or $\partial\mu_2/\partial x^\alpha$) between (6) and (12). Thus

$$- d\gamma = \left(\Delta_{\alpha\sigma}S - \frac{\Delta_{\alpha\sigma}V \, \Delta_{\alpha\beta}S}{\Delta_{\alpha\beta}V}\right) dT$$

$$+ \left\{\left(\Gamma_2 - \frac{x^\alpha \, \Gamma_1}{1 - x^\alpha}\right) + \frac{\Delta_{\alpha\sigma}V \, (x^\beta - x^\alpha)}{\Delta_{\alpha\beta}V \, (1 - x^\alpha)}\right\} \frac{\partial\mu_2}{\partial x^\alpha} \, dx^\alpha \qquad 5.\ 60.\ 17$$

If we vary the temperature and the pressure so as to maintain x^α constant, (17) becomes

$$- \frac{d\gamma}{dT} = \Delta_{\alpha\sigma}S - \frac{\Delta_{\alpha\sigma}V \, \Delta_{\alpha\beta}S}{\Delta_{\alpha\beta}V} \qquad \text{(const. } x^\alpha) \qquad 5.\ 60.\ 18$$

This formula applies in principle to any interface. For a liquid-vapour interface we may assume that $\Delta_{\alpha\sigma}V/\Delta_{\alpha\beta}V$ is negligibly small and then (18) reduces to

$$- \frac{d\gamma}{dT} = \Delta_{\alpha\sigma}S \qquad \text{(const. } x^\alpha) \qquad 5.\ 60.\ 19$$

which is the same as (5. 55. 1). For a liquid-liquid interface formula (18), though strictly correct is of little use since the ratio $\Delta_{\alpha\sigma}V/\Delta_{\alpha\beta}V$ of two very small quantities is difficult, if not impossible, to estimate or measure.

§ 5. 61 SOLID MIXTURES

We turn now to a brief consideration of solid mixtures, especially binary solid mixtures. Much of the treatment of liquid mixtures is directly applicable mutatis mutandis to solid mixtures. Other parts of the treatment are obviously not applicable, in particular osmotic equilibrium and interfacial tensions.

There is a further difference between the treatments of liquid and of solid mixtures, a difference of degree or of emphasis rather than of kind. Most liquids are sufficiently volatile to have a conveniently measurable vapour pressure. Hence the partial vapour pressures of a liquid mixture are familiar experimental quantities. There is consequently a natural and reasonable tendency so far as possible to express most other equilibrium properties in terms of the partial vapour pressures. Whereas some solids also have readily measurable vapour pressures, many are effectively involatile. This being so, there is no particular merit in expressing other equilibrium properties in terms of the partial vapour pressures rather than in terms of the absolute activities. If then we compare, for example, the Gibbs-Duhem formula for a binary mixture

$$(1 - x) \frac{\partial \mu_1}{\partial x} + x \frac{\partial \mu_2}{\partial x} = 0 \qquad 5. 61. 1$$

or its corollary

$$(1 - x) \frac{\partial \ln \lambda_1}{\partial x} + x \frac{\partial \ln \lambda_2}{\partial x} = 0 \qquad 5. 61. 2$$

with the Duhem-Margules relation

$$(1 - x) \frac{\partial \ln p_1}{\partial x} + x \frac{\partial \ln p_2}{\partial x} = 0 \qquad 5. 61. 3$$

whereas these three relations are all equivalent, it is natural to place the emphasis on (3) in the case of liquids, but on (1) or (2) in the case of solids.

One of the great similarities between solids and liquids, in contrast to gases, is their insensitivity to pressure. For most purposes we may ignore the pressure. When we do this, a single phase of two components has two degrees of freedom, so that we may use as independent variables T, x. A pair of such phases in equilibrium has then only one degree of freedom, the composition of both phases being determined by the temperature.

We shall deal extremely briefly with the aspects of solid solutions which are parallel to those of liquid solutions. We shall often quote formulae without repeating derivations previously given for liquids.

§ 5. 62 STATIONARY MELTING POINTS

In § 5. 25 we proved that whenever the relative compositions of a liquid and vapour in mutual equilibrium at a given pressure are identical, the equilibrium temperature is a minimum or maximum at the given pressure. By precisely the same proof the same result can be derived for a solid and vapour in equilibrium.

Of greater practical interest is the equilibrium between solid and liquid phases. Using the superscripts ^{S} and ^{L} to refer to these two phases respectively, we can derive a formula analogous to (5. 25. 8), namely

$$(S_m^L - S_m^S)\frac{dT}{dx} = (x^L - x^S)\left(\frac{\partial \mu_1}{\partial x} - \frac{\partial \mu_2}{\partial x}\right) \qquad 5.\ 62.\ 1$$

where x denotes the mole fraction of the component 2 in either phase. Whereas formula (5. 25. 8) was deduced for constant pressure conditions, as far as (1) is concerned the pressure is practically irrelevant. If the liquid and solid phases have identical relative compositions then

$$x^S = x^L \qquad 5.\ 62.\ 2$$

and so (1) reduces to

$$(S_m^L - S_m^S)\frac{dT}{dx} = 0 \qquad 5.\ 62.\ 3$$

Since $S_m^L \neq S_m^S$ it follows that

$$dT/dx = 0 \qquad 5.\ 62.\ 4$$

Thus when the relative compositions of the solid and liquid in mutual equilibrium are identical, the equilibrium temperature is stationary.

§ 5. 63 IDEAL MIXTURES

A solid *ideal mixture* is defined in the same manner as in the case of liquids, namely by

$$\Delta_m G = RT \Sigma_i x_i \ln x_i \qquad 5.\ 63.\ 1$$

and in particular for a binary ideal mixture

$$\Delta_m G/RT = (1 - x) \ln (1 - x) + x \ln x \qquad 5.\ 63.\ 2$$

From this definition it follows immediately for a binary mixture that

$$\lambda_1 = \lambda_1^0 (1 - x) \qquad \text{5. 63. 3}$$

$$\lambda_2 = \lambda_2^0 x \qquad \text{5. 63. 4}$$

where the superscript ^{0} denotes the pure solid phase. Actual examples of ideal mixtures are as few among solids as among liquids, but the ideal mixture remains the convenient standard with which to compare a real mixture.

The thermodynamic functions and properties of ideal mixtures follow directly from (1) or (2) as in the case of liquids. In particular the heat functions are additive; that is to say the molar heat of mixing is zero. On the other hand the *molar entropy of mixing* is given by

$$\Delta_m S/R = - (1 - x) \ln (1 - x) - x \ln x \qquad \text{5. 63. 5}$$

Probably the most important application of this and related formulae is to isotopes, as in § 4. 57.

§ 5. 64 NON-IDEAL MIXTURES

Any real mixture is conveniently compared with an ideal mixture either by the use of excess functions defined by

$$G_m^E = \Delta_m G - \Delta_m G^I \qquad \text{5. 64. 1}$$

and the like, or by the use of activity coefficients f_1, f_2 defined by

$$\lambda_1 = \lambda_1^0 (1 - x) f_1 \qquad \text{5. 64. 2}$$

$$\lambda_2 = \lambda_2^0 x f_2 \qquad \text{5. 64. 3}$$

According to the Gibbs-Duhem relation (5. 61. 2) the two activity coefficients are interrelated by

$$(1 - x) \frac{\partial \ln f_1}{\partial x} + x \frac{\partial \ln f_2}{\partial x} = 0 \qquad \text{5. 64. 4}$$

The temperature coefficients of the activity coefficients are related to the *partial molar heats of mixing* according to

$$\frac{\partial \ln f_1}{\partial T} = - \frac{H_1 - H_1^0}{RT^2} \qquad \text{(const. } x) \qquad \text{5. 64. 5}$$

$$\frac{\partial \ln f_2}{\partial T} = - \frac{H_2 - H_2^0}{RT^2} \qquad \text{(const. } x) \qquad \text{5. 64. 6}$$

The conditions for internal stability with respect to splitting into two phases, for the equilibrium between two phases and for the critical temperature of mixing are precisely analogous to those for liquid mixtures.

§ 5. 65 SIMPLE MIXTURES

We define a *simple solid mixture* in precisely the same way as a simple liquid mixture by (5. 44. 1)

$$G_m^E = x (1 - x) w \qquad 5.\ 65.\ 1$$

where w is independent of the composition but generally depends on the temperature. From 1 we deduce immediately

$$\ln f_1 = \frac{w}{RT} x^2 \qquad 5.\ 65.\ 2$$

$$\ln f_2 = \frac{w}{RT} (1 - x)^2 \qquad 5.\ 65.\ 3$$

The partial molar heats of mixing are given by

$$H_1 - H_1^0 = \left(w - T \frac{dw}{dT}\right) x^2 \qquad 5.\ 65.\ 4$$

$$H_2 - H_2^0 = \left(w - T \frac{dw}{dT}\right) (1 - x)^2 \qquad 5.\ 65.\ 5$$

If w is positive, the temperature of critical mixing T_c is given by

$$T_c = \tfrac{1}{2} w/R \qquad 5.\ 65.\ 6$$

If on the other hand w is negative, the temperature T_λ determined by

$$T_\lambda = - \tfrac{1}{2} w/R \qquad 5.\ 65.\ 7$$

is likewise of interest as the highest temperature at which what is called *long-range order* can persist. We merely mention this in passing, because of the formal similarity between (6) and (7). We shall revert to the subject in § 7. 20 and § 7. 21 where we shall see that the temperature given by (7) is under certain conditions that of a *transition of the second order*.

SOLUTIONS, ESPECIALLY DILUTE SOLUTIONS

§ 6. 01 INTRODUCTION

There is no fundamental difference between a liquid mixture and a solution. The difference is in the manner of description. In the description of mixtures in the previous chapter all the constituent species were treated in a like manner. In the description of *solutions* in the present chapter, we shall on the contrary single out one species which we call the *solvent*. All the remaining species are called *solutes*. There is no rigid rule to determine which species shall be regarded as solvent, but it is usually the species present in the highest proportion, at least among those species which are liquid in the pure state at the given temperature and pressure. For example we should at room temperature speak of water as solvent and urea as solute, even if the urea were in excess, because pure urea at room temperature is a solid.

We shall always denote the solvent by the subscript $_1$ and the solutes by the subscripts $_{2, 3, }\ldots$ in particular or by the general subscript $_s$.

§ 6. 02 MOLE RATIOS AND MOLALITIES

We consider a phase containing n_1 units of the species 1, n_2 units of the species 2 and so on. When considering such a phase as a mixture we described the composition by the fractions $n_1/\Sigma_i n_i$, $n_2/\Sigma_i n_i$ and so on. When considering this phase as a solution we shall on the contrary describe its composition by the ratios n_2/n_1, n_3/n_1 and so on.

In particular if we choose as unit of quantity of each species the mole, then while the fractions $n_1/\Sigma_i n_i$, $n_2/\Sigma_i n_i$, $\ldots$ were denoted by x_1, x_2, $\ldots$ and were called mole fractions, the fractions n_2/n_1, n_3/n_1, $\ldots$ will be denoted by r_2, r_3, $\ldots$ and will be called *mole ratios*. In a phase of c component species there are c different mole fractions, which we recall are related by $\Sigma_i x_i = 1$ so that only $c - 1$ are independent. There are only $c - 1$ mole ratios r_2, r_3, $\ldots$ r_c and these are all independent. We may use these as the independent variables together with T and P.

For all purposes of general theory we shall use the variables r_2, r_3, ... r_c together with T, P. For practical purposes it is customary to use instead of r_s a quantity m_s directly proportional to r_s defined by

$$m_s = \frac{r_s}{M_1} \qquad 6.\,02.\,1$$

where M_1 denotes the molar mass of the solvent species 1. Moreover it is customary practice to express M_1 in kg mole^{-1} so that m_s is measured in moles of solute per kilogram of solvent. This quantity m_s is called *molality*. We shall derive most of our formulae in terms of the mole ratios r and shall transcribe only a few important ones into terms of molalities m by use of (1). The mole fractions x and mole ratios r are interrelated by

$$r_2 = \frac{x_2}{x_1} = \frac{x_2}{1 - \Sigma_s x_s} \qquad 6.\,02.\,2$$

$$x_2 = \frac{r_2}{1 + \Sigma_s r_s} \qquad 6.\,02.\,3$$

and similar relations for the other solute species. We also note the relation

$$(1 + \Sigma_s r_s)\,(1 - \Sigma_s x_s) = 1 \qquad 6.\,02.\,4$$

§ 6. 03 NOTATION FOR CHANGES OF COMPOSITION

When we choose as independent variables T, P, r_s the most general variation of an intensive property I has the form

$$dI = \frac{\partial I}{\partial T}\,dT + \frac{\partial I}{\partial P}\,dP + \Sigma_s \frac{\partial I}{\partial r_s}\,dr_s \qquad 6.\,03.\,1$$

It will sometimes be convenient to use the abbreviation DI defined by

$$DI = \Sigma_s \frac{\partial I}{\partial r_s}\,dr_s \qquad 6.\,03.\,2$$

In this notation (1) becomes

$$dI = \frac{\partial I}{\partial T}\,dT + \frac{\partial I}{\partial P}\,dP + DI \qquad 6.\,03.\,3$$

When there is only one solute species (2) reduces to

$$DI = \frac{\partial I}{\partial r}\,dr \qquad 6.\,03.\,4$$

and the abbreviation becomes redundant.

§ 6. 04 PARTIAL AND APPARENT VOLUMES

We recall the definition (5. 05. 10) of partial volumes

$$V_1 = \left(\frac{\partial V}{\partial n_1}\right)_{T, P, n_2, n_3, \cdots} \qquad \text{6. 04. 1}$$

$$V_2 = \left(\frac{\partial V}{\partial n_2}\right)_{T, P, n_1, n_3, \cdots} \qquad \text{6. 04. 2}$$

and the relation (5. 08. 4) between them at constant temperature and pressure

$$n_1 D V_1 + \Sigma_s n_s D V_s = 0 \qquad \text{6. 04. 3}$$

Dividing (3) by n_1 we obtain

$$D V_1 + \Sigma_s r_s D V_s = 0 \qquad \text{6. 04. 4}$$

In particular when there is only one solute (4) becomes

$$\frac{\partial V_1}{\partial r} + r \frac{\partial V_2}{\partial r} = 0 \qquad \text{6. 04. 5}$$

When there is only one solute species 2 the quantity V_q defined by

$$n_2 V_\varphi = V - n_1 V_1^0 \qquad \text{6. 04. 6}$$

where V_1^0 denotes the molar volume of the pure solvent, is called the *apparent molar volume* of the solute. We can obtain the relation between the apparent molar volume V_φ and the partial molar volume V_2 by differentiating (6) with respect to n_2 keeping n_1 constant. We find

$$V_2 = \frac{\partial V}{\partial n_2} = V_\varphi + n_2 \left(\frac{\partial V_\varphi}{\partial n_2}\right)_{n_1} = V_\varphi + r \frac{\partial V_\varphi}{\partial r} = V_q + m \frac{\partial V_q}{\partial m}$$

$$\text{6. 04. 7}$$

There are no such quantities as V_φ when there is more than one solute species.

§ 6. 05 OTHER PARTIAL QUANTITIES

All that has been said in the previous section about partial volume applies mutatis mutandis to other partial quantities. We recall the relations of § 5. 07 between the various kinds of partial quantities. These relations apply both to the partial quantities of the solvent and to those of the solute.

We also recall the important equality (5. 11. 3) which holds both for the solvent species and for the solute species

$$\mu_1 = G_1 \qquad\qquad \mu_s = G_s \qquad\qquad \text{6. 05. 1}$$

with the consequent relations

$$\frac{\partial \mu_1}{\partial P} = V_1 \qquad\qquad \frac{\partial \mu_s}{\partial P} = V_s \qquad\qquad \text{6. 05. 2}$$

$$\frac{\partial \mu_1}{\partial T} = -S_1 \qquad\qquad \frac{\partial \mu_s}{\partial T} = -S_s \qquad\qquad \text{6. 05. 3}$$

$$\frac{\partial \ln \lambda_1}{\partial T} = -\frac{H_1}{RT^2} \qquad\qquad \frac{\partial \ln \lambda_s}{\partial T} = -\frac{H_s}{RT^2} \qquad\qquad \text{6. 05. 4}$$

§ 6. 06 GIBBS-DUHEM RELATION

We recall the Gibbs-Duhem relation (5. 11. 4). When we divide through by n_1 we obtain the alternative form

$$D\mu_1 + \Sigma_s\, r_s\, D\mu_s = 0 \qquad\qquad \text{6. 06. 1}$$

or in the case of a single solute

$$\frac{\partial \mu_1}{\partial r} + r\,\frac{\partial \mu_2}{\partial r} = 0 \qquad\qquad \text{6. 06. 2}$$

We can also write (1) in terms of absolute activities

$$D \ln \lambda_1 + \Sigma_s\, r_s\, D \ln \lambda_s = 0 \qquad\qquad \text{6. 06. 3}$$

or in the case of a single solute

$$\frac{\partial \ln \lambda_1}{\partial r} + r\,\frac{\partial \ln \lambda_2}{\partial r} = 0 \qquad\qquad \text{6. 06. 4}$$

§ 6. 07 PARTIAL QUANTITIES AT HIGH DILUTION

If X denotes any extensive quantity so that X_1, X_2 are the corresponding partial quantities of solvent and solute in a solution containing only one solute, then we have relations analogous to (6. 04. 5)

$$\frac{\partial X_1}{\partial r} + r\,\frac{\partial X_2}{\partial r} = 0 \qquad\qquad \text{6. 07. 1}$$

It follows that when $r \to 0$ either $\partial X_1/\partial r \to 0$ or $\partial X_2/\partial r \to \infty$. The

former case occurs when X denotes V or U or H; the latter occurs when X denotes S or F or G. This will become clear from the formulae of § 6. 09.

§ 6. 08 IDEAL DILUTE SOLUTIONS

Let us consider a solution of a volatile solute 2 in the solvent 1 so dilute that $n_2 \ll n_1$. It is then physically obvious that the partial vapour pressure of 2 will be directly proportional to n_2, that is to say

$$p_2 \propto n_2 \qquad \qquad 6.\,08.\,1$$

This however raises the question whether the proportionality (1) holds at constant $n_1 + n_2$, that is to say

$$p_2 \propto x_2 \qquad \qquad 6.\,08.\,2$$

or at constant n_1, that is to say

$$p_2 \propto r_2 \qquad \qquad 6.\,08.\,3$$

The answer is that in the limit as x_2 and r_2 tend to zero (2) and (3) become equivalent and it is only in this limit that either is obviously true. At finite values of x_2 and r_2 we must not expect either (2) or (3) to be accurate, but we may use either as a basis for comparison with the actual behaviour of solutions. It is true that (2) can under favourable conditions hold for all values of x from 0 to 1 in which case we have an ideal mixture as described in § 5. 29. Formula (3) on the contrary becomes untenable as we approach the state of the pure liquid 2, when $r_2 \to \infty$, since it would lead to the absurd conclusion that p_2^0 is infinite. We must however remember that in this chapter our convention that the species 1 is the solvent implies that this species is present in excess and we are consequently not concerned with conditions approaching that of the pure liquid 2. In fact we are concerned mainly with the condition $r_2 \ll 1$. Bearing in mind this implied restriction we are free to choose either (2) or (3) as a basis of comparison with actual behaviour. In practice it has been found that (3) is more convenient than (2) because the value of r_2 is unaffected by the addition to a given solution of other solute species. This practical advantage will become clearer in the next chapter when we consider chemical reactions between solute species.

We shall accordingly choose as a basis of comparison with actual behaviour formula (3) after we have generalized it in two respects.

In the first place we need not restrict ourselves to only one solute species and we accordingly replace (3) by the more general relation

$$p_s \propto r_s \qquad \text{(all } s) \qquad \text{6. 08. 4}$$

In the second place it is clear from the relations of § 5. 19 that (4) is equivalent to

$$\lambda_s \propto r_s \qquad \text{(all } s) \qquad \text{6. 08. 5}$$

and (5) is applicable to solute species of immeasurably low volatility. We shall now adopt (5) as our basis of comparison with actual behaviour and we define a solution as being *ideal dilute* when the proportionality (5) is obeyed for all values of r_s less than or equal to that of the solution under consideration.

We can write (5) in the alternative form

$$\lambda_s = \lambda_s^\infty r_s \qquad \text{(all } s) \qquad \text{6. 08. 6}$$

where λ_s^∞ depends on the nature of the solute, the nature of the solvent, the temperature and the pressure, but not on the mole ratio r_s of the solute considered nor on the mole ratio of any other solute species. In numerical applications, as opposed to general theory, it is customary to use molalities instead of mole ratios. We then replace (6) by

$$\lambda_s = \lambda_s^\ominus m_s \qquad \text{(all } s) \qquad \text{6. 08. 7}$$

where

$$\lambda_s^\ominus = \lambda_s^\infty M_1 \qquad \text{6. 08. 8}$$

in which M_1 is the molar mass of the solvent (usually measured in kilograms per mole).

Finally we may, if we prefer it, use chemical potentials instead of absolute activities. We then have in analogous notation

$$\mu_s = \mu_s^\infty + RT \ln r_s \qquad \text{6. 08. 9}$$

$$\mu_s = \mu_s^\ominus + RT \ln m_s \qquad \text{6. 08. 10}$$

$$\mu_s^\ominus = \mu_s^\infty + RT \ln M_1 \qquad \text{6. 08. 11}$$

$\vee$

§ 6. 09 THERMODYNAMIC FUNCTIONS OF IDEAL DILUTE SOLUTIONS

Having defined an ideal dilute solution in terms of the absolute activities or chemical potentials of the solute species, we can deduce

the relations for the properties of the solvent by means of the Gibbs-Duhem relation (6. 06. 3)

$$D \ln \lambda_1 + \Sigma_s r_s \, D \ln \lambda_s = 0 \qquad \text{6. 09. 1}$$

From (6. 08. 6) we have

$$r_s \, D \ln \lambda_s = r_s \, D \ln r_s = Dr_s \qquad \text{6. 09. 2}$$

Substituting (2) into (1) we obtain

$$D \ln \lambda_1 = - \Sigma_s \, Dr_s = - D \Sigma_s \, r_s \qquad \text{6. 09. 3}$$

and so by integration

$$\ln \frac{\lambda_1}{\lambda_1^0} = - \Sigma_s \, r_s \qquad \text{6. 09. 4}$$

where as usual the superscript ^{0} denotes the value for the pure liquid. We can rewrite (4) in terms of chemical potentials

$$\mu_1 = \mu_1^0 - RT \, \Sigma_s \, r_s \qquad \text{6. 09. 5}$$

and in terms of vapour pressures or strictly fugacities

$$\ln \frac{p_1}{p_1^0} = - \Sigma_s \, r_s \qquad \text{6. 09. 6}$$

By use of (6. 05. 2) we deduce

$$V_1 = V_1^0 \qquad \text{6. 09. 7}$$

$$V_s = V_s^\infty \qquad \text{6. 09. 8}$$

where V_s^∞ denotes the limiting value of V_s at infinite dilution of all solute species. We see then that V_1 and V_s are in an ideal dilute solution in a given solvent independent of the composition.

By use of (6. 05. 3) we deduce

$$S_1 = S_1^0 + R \, \Sigma_s \, r_s \qquad \text{6. 09. 9}$$

$$S_s = S_s^\infty - R \ln r_s \qquad \text{6. 09. 10}$$

where

$$S_s^\infty = - \frac{\partial \mu_s^\infty}{\partial T} \qquad \text{6. 09. 11}$$

and is thus in an ideal dilute solution in a given solvent independent of the composition.

By use of (6. 05. 4) we deduce

$$H_1 = H_1^0 \qquad\qquad\qquad 6.\,09.\,12$$

$$H_s = H_s^\infty \qquad\qquad\qquad 6.\,09.\,13$$

where H_s^∞ denotes the limiting value of H_s at infinite dilution of all solute species.

It follows from (7), (8) and from (12), (13) that any two ideal dilute solutions in the same solvent mix at constant temperature and pressure without change of volume and without gain or loss of heat.

§ 6. 10 REAL SOLUTIONS

As already mentioned, we do not expect a real solution to be ideal dilute except in the limit of infinite dilution but it is convenient to compare the behaviour of any real solution with its hypothetical behaviour if it remained ideal dilute at all compositions extending from infinite dilution to its actual composition. We then express the deviations between the real behaviour and this hypothetical behaviour by means of certain coefficients as will be described in the succeeding sections.

§ 6. 11 ACTIVITY COEFFICIENTS OF SOLUTE SPECIES

We define the *activity coefficient* γ_2 of the solute species 2 by the relations

$$\lambda_2 = \lambda_2^\infty r_2 \gamma_2 = \lambda_2^\ominus m_2 \gamma_2 \qquad\qquad 6.\,11.\,1$$

$$\gamma_2 \to 1 \qquad \text{as all } m_s \to 0 \qquad\qquad 6.\,11.\,2$$

Alternatively we may express (1) in terms of chemical potentials

$$\mu_2 = \mu_2^\infty + RT \ln r_2 \gamma_2 = \mu_2^\ominus + RT \ln m_2 \gamma_2 \qquad 6.\,11.\,3$$

in conjunction with (2). It is clear that the deviation of γ_2 from one or of $\ln \gamma_2$ from zero is a measure of deviation from an ideal dilute solution.

It need hardly be mentioned that similar relations hold for every solute species. Thus (1) may be generalized to

$$\lambda_s = \lambda_s^\infty r_s \gamma_s = \lambda_s^\ominus m_s \gamma_s \qquad\qquad 6.\,11.\,4$$

and (3) to

$$\mu_s = \mu_s^\infty + RT \ln r_s \gamma_s = \mu_s^\ominus + RT \ln m_s \gamma_s \qquad 6.\,11.\,5$$

These activity coefficients γ seem to have been first used by Noyes

and Bray *, who however attribute them to G. N. Lewis by whom they were extensively used †. It is unfortunate that the same name activity coefficient is used both for these γ's and for the f's of the previous chapter. The name is however so well established for both that there seems little prospect of its being dropped for either. In the present book the distinction is always clear from the different symbols, but not all authors use these two symbols in precisely this way. The following names avoid ambiguity but neither of them has the merit of conciseness

f activity coefficient (Hildebrand)   ￼

γ activity coefficient (Lewis) ￼

§ 6. 12 OSMOTIC COEFFICIENT OF SOLVENT

Following Bjerrum ‡ we define the osmotic coefficient φ of the solvent by

$$\ln \frac{\lambda_1}{\lambda_1^0} = \ln \frac{p_1}{p_1^0} = - \varphi \, \Sigma_s \, r_s \qquad 6.\,12.\,1$$

By comparing (1) with (6. 09. 4) we see that $\varphi - 1$ is a measure of deviation of behaviour from that of an ideal dilute solution.

We can also write (1) in terms of chemical potentials as

$$\mu_1 = \mu_1^0 - RT\varphi \, \Sigma_s \, r_s \qquad 6.\,12.\,2$$

§ 6. 13 RELATION BETWEEN ACTIVITY COEFFICIENTS AND OSMOTIC COEFFICIENT

When we substitute (6. 12. 1) and (6. 11. 4) into the Gibbs-Duhem relation (6. 06. 3) we obtain

$$D \, (\varphi \, \Sigma_s \, r_s) = \Sigma_s \, r_s \, D \, (\ln r_s \, \gamma_s) \qquad 6.\,13.\,1$$

which can be rewritten as

$$D \, \{(\varphi - 1) \, \Sigma_s \, r_s\} = \Sigma_s \, r_s \, D \ln \gamma_s \qquad 6.\,13.\,2$$

a relation due to Bjerrum §. In the case of a single solute species (2) reduces to

$$\frac{\partial}{\partial r} \{(\varphi - 1) \, r\} = r \frac{\partial \ln \gamma}{\partial r} \qquad 6.\,13.\,3$$

or

$$\frac{\varphi - 1}{r} + \frac{\partial \varphi}{\partial r} = \frac{\partial \ln \gamma}{\partial r} \qquad 6.\,13.\,4$$

* Noyes and Bray, *J. Amer. Chem. Soc.* 1911 **33** 1646.

† Lewis and Randall, *Thermodynamics and the Free Energy of Chemical Substances* 1923.

‡ Bjerrum, *Fysisk Tidskr.* 1916 **15** 66, *Z. Electrochem* 1918 **24** 325.

§ Bjerrum, *Z. phys Chem.* 1923 **104** 406.

If for example φ is related to r by

$$\varphi - 1 = A r^n \qquad (A, n \text{ const.}) \qquad 6.\,13.\,5$$

then by substituting from (5) into (4) we obtain after integration

$$\ln \gamma = \frac{n+1}{n} A r^n \qquad 6.\,13.\,6$$

§ 6. 14 TEMPERATURE DEPENDENCE

By substitution of (6. 11. 4) into the second of equations (6. 05. 4) we obtain

$$\frac{\partial \ln \lambda_s^\infty}{\partial T} + \frac{\partial \ln \gamma_s}{\partial T} = -\frac{H_s}{RT^2} \qquad 6.\,14.\,1$$

In the limit of infinite dilution (1) reduces to

$$\frac{\partial \ln \lambda_s^\infty}{\partial T} = -\frac{H_s^\infty}{RT^2} \qquad 6.\,14.\,2$$

Subtracting (2) from (1) we obtain for the temperature dependence of the activity coefficient

$$\frac{\partial \ln \gamma_s}{\partial T} = -\frac{H_s - H_s^\infty}{RT^2} \qquad 6.\,14.\,3$$

In particular we observe that γ_s will be independent of temperature if H_s is independent of composition.

By substitution of (6. 12. 1) into the first of equations (6. 05. 4) we obtain

$$-\frac{\partial \varphi}{\partial T} \Sigma_s r_s + \frac{\partial \ln \lambda_1^0}{\partial T} = -\frac{H_1}{RT^2} \qquad 6.\,14.\,4$$

For the pure solvent (4) reduces to

$$\frac{\partial \ln \lambda_1^0}{\partial T} = -\frac{H_1^0}{RT^2} \qquad 6.\,14.\,5$$

By subtraction of (5) from (4) we find for the temperature dependence of the osmotic coefficient

$$\frac{\partial \varphi}{\partial T} \Sigma_s r_s = \frac{H_1 - H_1^0}{RT^2} \qquad 6.\,14.\,6$$

In particular we observe that φ will be independent of temperature if H_1 is independent of composition.

§ 6. 15 PRESSURE DEPENDENCE

By substitution of (6. 11. 5) into the second of equations (6. 05. 2) we obtain

$$\frac{\partial \mu_s^\infty}{\partial P} + RT \frac{\partial \ln \gamma_s}{\partial P} = V_s \qquad 6. 15. 1$$

In the limit of infinite dilution (1) reduces to

$$\frac{\partial \mu_s^\infty}{\partial P} = V_s^\infty \qquad 6. 15. 2$$

By subtraction of (2) from (1) we find for the pressure dependence of the activity coefficient

$$\frac{\partial \ln \gamma_s}{\partial P} = \frac{V_s - V_s^\infty}{RT} \qquad 6. 15. 3$$

By substitution of (6. 12. 2) into the first of equations (6. 05. 2) we obtain

$$- RT \frac{\partial \varphi}{\partial P} \Sigma_s r_s + \frac{\partial \mu_1^0}{\partial P} = V_1 \qquad 6. 15. 4$$

For the pure solvent (4) reduces to

$$\frac{\partial \mu_1^0}{\partial P} = V_1^0 \qquad 6. 15. 5$$

By subtraction of (5) from (4) we obtain for the pressure dependence of the osmotic coefficient

$$\frac{\partial \varphi}{\partial P} \Sigma_s r_s = - \frac{V_1 - V_1^0}{RT} \qquad 6. 15. 6$$

All these pressure dependences are usually negligible except at high pressures.

§ 6. 16 VAPOUR PRESSURE OF SOLVENT

From (6. 12. 1) we have

$$\ln \frac{p_1}{p_1^0} = - \varphi \Sigma_s r_s \qquad 6. 16. 1$$

If for example φ is related to r by

$$\varphi - 1 = A r^n \qquad (A, n \text{ const.}) \qquad 6.13.5$$

then by substituting from (5) into (4) we obtain after integration

$$\ln \gamma = \frac{n+1}{n} A r^n \qquad 6.13.6$$

§ 6.14 TEMPERATURE DEPENDENCE

By substitution of (6.11.4) into the second of equations (6.05.4) we obtain

$$\frac{\partial \ln \lambda_s^\infty}{\partial T} + \frac{\partial \ln \gamma_s}{\partial T} = -\frac{H_s}{RT^2} \qquad 6.14.1$$

In the limit of infinite dilution (1) reduces to

$$\frac{\partial \ln \lambda_s^\infty}{\partial T} = -\frac{H_s^\infty}{RT^2} \qquad 6.14.2$$

Subtracting (2) from (1) we obtain for the temperature dependence of the activity coefficient

$$\frac{\partial \ln \gamma_s}{\partial T} = -\frac{H_s - H_s^\infty}{RT^2} \qquad 6.14.3$$

In particular we observe that γ_s will be independent of temperature if H_s is independent of composition.

By substitution of (6.12.1) into the first of equations (6.05.4) we obtain

$$-\frac{\partial \varphi}{\partial T} \Sigma_s r_s + \frac{\partial \ln \lambda_1^0}{\partial T} = -\frac{H_1}{RT^2} \qquad 6.14.4$$

For the pure solvent (4) reduces to

$$\frac{\partial \ln \lambda_1^0}{\partial T} = -\frac{H_1^0}{RT^2} \qquad 6.14.5$$

By subtraction of (5) from (4) we find for the temperature dependence of the osmotic coefficient

$$\frac{\partial \varphi}{\partial T} \Sigma_s r_s = \frac{H_1 - H_1^0}{RT^2} \qquad 6.14.6$$

In particular we observe that φ will be independent of temperature if H_1 is independent of composition.

§ 6.15 PRESSURE DEPENDENCE

By substitution of (6.11.5) into the second of equations (6.05.2) we obtain

$$\frac{\partial \mu_s^\infty}{\partial P} + RT \frac{\partial \ln \gamma_s}{\partial P} = V_s \qquad 6.15.1$$

In the limit of infinite dilution (1) reduces to

$$\frac{\partial \mu_s^\infty}{\partial P} = V_s^\infty \qquad 6.15.2$$

By subtraction of (2) from (1) we find for the pressure dependence of the activity coefficient

$$\frac{\partial \ln \gamma_s}{\partial P} = \frac{V_s - V_s^\infty}{RT} \qquad 6.15.3$$

By substitution of (6.12.2) into the first of equations (6.05.2) we obtain

$$-RT \frac{\partial \varphi}{\partial P} \Sigma_s r_s + \frac{\partial \mu_1^0}{\partial P} = V_1 \qquad 6.15.4$$

For the pure solvent (4) reduces to

$$\frac{\partial \mu_1^0}{\partial P} = V_1^0 \qquad 6.15.5$$

By subtraction of (5) from (4) we obtain for the pressure dependence of the osmotic coefficient

$$\frac{\partial \varphi}{\partial P} \Sigma_s r_s = -\frac{V_1 - V_1^0}{RT} \qquad 6.15.6$$

All these pressure dependences are usually negligible except at high pressures.

§ 6.16 VAPOUR PRESSURE OF SOLVENT

From (6.12.1) we have

$$\ln \frac{p_1}{p_1^0} = -\varphi \Sigma_s r_s \qquad 6.16.1$$

Differentiating (1) with respect to T and using (6. 14. 6) we obtain for a solution of given composition

$$\frac{\partial}{\partial T}\left(\ln \frac{p_1}{p_1^0}\right) = -\frac{\partial \varphi}{\partial T} \Sigma_s r_s = -\frac{H_1 - H_1^0}{RT^2} \qquad 6.\ 16.\ 2$$

§ 6. 17 VAPOUR PRESSURE OF SOLUTE

For a volatile solute species we may replace (6. 11. 4) by

$$p_s = p_s^\infty r_s \gamma_s = p_s^\ominus m_s \gamma_s \qquad 6.\ 17.\ 1$$

where p_s^∞, $p_s^\ominus$ are independent of the composition but depend on the nature of the solute s and the solvent. Differentiating (1) with respect to T and using (6. 14. 3) we obtain

$$\frac{\partial}{\partial T}\left(\ln \frac{p_s}{p_s^\infty}\right) = \frac{\partial}{\partial T}\left(\ln \frac{p_s}{p_s^\ominus}\right) = \frac{\partial \ln \gamma_s}{\partial T} = -\frac{H_s - H_s^\infty}{RT^2} \qquad 6.\ 17.\ 2$$

§ 6. 18 OSMOTIC PRESSURE

We recall formula (5. 27. 8)

$$\frac{\Pi[V_1]}{RT} = \ln \frac{p_1^0}{p_1} \qquad 6.\ 18.\ 1$$

where $[V_1]$ denotes the value of V_1 at a pressure equal to the mean of the pressure P on the pure solvent and the pressure $P + \Pi$ on the solution at osmotic equilibrium while both p_1 and p_1^0 are values at an external pressure P. Since formula (1) does not contain mole fractions it is equally applicable to solutions described in terms of mole ratios.

Substituting (6. 12. 1) into (1) we obtain

$$\frac{\Pi[V_1]}{RT} = \varphi \Sigma_s r_s \qquad 6.\ 18.\ 2$$

If we use the superscript id to denote a hypothetical ideal dilute solution with the same composition as the actual solution we have

$$\frac{\Pi^{id}[V_1]}{RT} = \Sigma_s r_s \qquad 6.\ 18.\ 3$$

Dividing (2) by (3) we find

$$\Pi = \varphi \Pi^{id} \qquad 6.\ 18.\ 4$$

and this relation explains the origin of the name *osmotic coefficient*.

§ 6. 19 FREEZING POINT

Let us now consider the equilibrium between the liquid solution and the pure solid solvent 1. We assume that the pressure is either constant or irrelevant. We use the superscript ^{s} to denote the solid phase, the superscript ^{0} for the pure liquid and no superscript for the liquid mixture. Then for equilibrium between the pure solid and the liquid mixture at its freezing point temperature T

$$\lambda_1 (T) = \lambda_1^s (T) \qquad \text{6. 19. 1}$$

If T^0 denotes the corresponding equilibrium temperature for the pure liquid, that is to say the freezing point of the pure liquid, we have correspondingly

$$\lambda_1^0 (T^0) = \lambda_1^s (T^0) \qquad \text{6. 19. 2}$$

Dividing (2) by (1) we obtain

$$\frac{\lambda_1^0 (T^0)}{\lambda_1 (T)} = \frac{\lambda_1^s (T^0)}{\lambda_1^s (T)} \qquad \text{6. 19. 3}$$

which can be rewritten in the form

$$\frac{\lambda_1^0 (T)}{\lambda_1 (T)} = \frac{\lambda_1^0 (T)}{\lambda_1^0 (T^0)} \frac{\lambda_1^s (T^0)}{\lambda_1^s (T)} \qquad \text{6. 19. 4}$$

Taking logarithms we have

$$\ln \frac{\lambda_1^0 (T)}{\lambda_1 (T)} = \ln \frac{\lambda_1^0 (T)}{\lambda_1^0 (T^0)} - \ln \frac{\lambda_1^s (T)}{\lambda_1^s (T^0)} \qquad \text{6. 19. 5}$$

Now applying the relation (6. 05. 4)

$$\frac{\partial \ln \lambda_1}{\partial T} = - \frac{H_1}{RT^2} \qquad \text{6. 19. 6}$$

to the pure solid and pure liquid in turn and integrating we obtain

$$\ln \frac{\lambda_1^s (T)}{\lambda_1^s (T^0)} = - \int_{T^0}^{T} \frac{H_1^s}{RT^2} \, dT \qquad \text{6. 19. 7}$$

$$\ln \frac{\lambda_1^0 (T)}{\lambda_1^0 (T^0)} = - \int_{T^0}^{T} \frac{H_1^0}{RT^2} \, dT \qquad \text{6. 19. 8}$$

Substituting (7) and (8) into (5) we obtain

$$\ln \frac{\lambda_1^0 (T)}{\lambda_1 (T)} = - \int_{T^0}^{T} \frac{H_1^0 - H_1^s}{RT^2} \, dT = - \int_{T^0}^{T} \frac{\Delta_f H_1^0}{RT^2} \, dT \qquad \text{6. 19. 9}$$

where $\Delta_f H_1^0$ is the molar heat of fusion of the pure solvent. We now substitute (6. 12. 1) into (9) and obtain

$$\varphi \, \Sigma_s \, r_s = - \int_{T^0}^{T} \frac{\Delta_f H_1^0}{R T^2} \, \mathrm{d}T \qquad \qquad 6. \ 19. \ 10$$

where φ denotes the osmotic coefficient of the solution at its freezing point.

We can rewrite (10) in the simpler form

$$\varphi \, \Sigma_s \, r_s = \frac{[\Delta_f H_1^0]}{R} \left(\frac{1}{T} - \frac{1}{T^0} \right) \qquad \qquad 6. \ 19. \ 11$$

where $[\Delta_f H_1^0]$ denotes the average value of $\Delta_f H_1^0$ over the reciprocal temperature interval $1/T^0$ to $1/T$. Since $\Delta_f H_1^0$ is always positive it follows that $T < T^0$. Thus the freezing point of the solution is always below that of the pure solvent if the solid phase is pure solvent.

We can rewrite (11) in terms of molalities as

$$\varphi \, \Sigma_s \, m_s = \frac{[\Delta_f H_1^0]}{R M_1} \left(\frac{1}{T} - \frac{1}{T^0} \right) \qquad \qquad 6. \ 19. \ 12$$

where M_1 denotes the molar mass of the solvent, usually measured in kg mole^{-1}. For dilute solutions when $T^0 - T \ll T^0$ we may replace (12) by the approximation

$$\varphi \, \Sigma_s \, m_s = \frac{\Delta_f H_1^0}{R T^{02} M_1} (T^0 - T) \qquad \qquad 6. \ 19. \ 13$$

or

$$T^0 - T = \frac{R T^{02} M_1}{\Delta_f H_1^0} \varphi \, \Sigma_s \, m_s \qquad \qquad 6. \ 19. \ 14$$

For water we have $\Delta_f H_1^0 / M_1 = 333.5 \text{ J g}^{-1}$
$$R T^0 = 2.2712 \times 10^3 \text{ J mole}^{-1}$$
$$T^0 = 273.15 \text{ deg}$$

so that the so-called *cryoscopic constant*

$$\frac{R T^{02} M_1}{\Delta_f H_1^0} = \frac{2.2712 \times 10^3 \times 273.15}{333.5 \times 10^3} \text{ deg mole}^{-1} \text{ kg}$$

$$= 1.860 \text{ deg mole}^{-1} \text{ kg}$$

§ 6. 20 BOILING POINT

We shall now consider the equilibrium between the liquid solution and the gas phase in the case that all the solute species have negligible vapour pressure. We accordingly regard the gas phase as consisting entirely of the component 1 and we use the superscript ^{G} to denote this phase.

We then proceed to consider the equilibrium between the two phases at a given pressure precisely as in the case of equilibrium with a pure solid phase studied in the previous section. The steps of the argument are precisely analogous and we obtain eventually the relation

$$\varphi \, \Sigma_s \, r_s = \frac{[\Delta_e H_1^0]}{R} \left(\frac{1}{T^0} - \frac{1}{T} \right) \qquad \text{6. 20. 1}$$

where $[\Delta_e H_1^0]$ denotes the value of the molar heat of evaporation $\Delta_e H_1^0$ for the pure liquid averaged over the reciprocal temperature interval $1/T$ to $1/T^0$ and φ is the osmotic coefficient at the boiling point of the solution. Since $\Delta_e H_1^0$ is always positive it follows that $T > T^0$. Thus the boiling point of any solution of non-votatile solutes is above that of the pure solvent.

We can rewrite (1) in terms of molalities as

$$\varphi \, \Sigma_s \, m_s = \frac{[\Delta_e H_1^0]}{R M_1} \left(\frac{1}{T^0} - \frac{1}{T} \right) \qquad \text{6. 20. 2}$$

where M_1 denotes the molar mass of the solvent, usually measured in kg mole^{-1}. For dilute solutions when $T - T^0 \ll T^0$ we may replace (2) by the approximation

$$\varphi \, \Sigma_s \, m_s = \frac{\Delta_e H_1^0}{R T^{02} M_1} (T - T^0) \qquad \text{6. 20. 3}$$

or

$$T - T^0 = \frac{R T^{02} M_1}{\Delta_e H_1^0} \varphi \, \Sigma_s \, m_s \qquad \text{6. 20. 4}$$

For water we have $\Delta_e H_1 / M_1 = 2256.7$ J g^{-1}
$$R = 8.3147 \text{ J deg}^{-1} \text{ mole}^{-1}$$
$$T^0 = 373.15 \text{ deg}$$

so that the so-called *ebullioscopic constant*

$$\frac{R T^{02} M_1}{\Delta_e H_1^0} = \frac{8.3147 \times 373.15 \times 373.15}{2256.7 \times 10^3} \text{ deg mole}^{-1} \text{ kg}$$

$$= 0.513 \text{ deg mole}^{-1} \text{ kg}$$

§ 6. 21 DISTRIBUTION BETWEEN TWO SOLVENTS

For the equilibrium of a solute species s between two solutions in different solvents we have

$$\lambda_s^\alpha = \lambda_s^\beta \qquad\qquad 6.\,21.\,1$$

where the superscripts α and β relate to the two phases. Substituting from (6. 11. 4) into (1) we obtain

$$\lambda_s^{\ominus\alpha} m_s^\alpha \gamma_s^\alpha = \lambda_s^{\ominus\beta} m_s^\beta \gamma_s^\beta \qquad\qquad 6.\,21.\,2$$

or by rearrangement

$$\frac{m_s^\beta \gamma_s^\beta}{m_s^\alpha \gamma_s^\alpha} = l_s^{\alpha\beta} \qquad\qquad 6.\,21.\,3$$

where $l_s^{\alpha\beta}$ is independent of the composition of the two phases and is defined by

$$l_s^{\alpha\beta} = \lambda_s^{\ominus\alpha}/\lambda_s^{\ominus\beta} \qquad\qquad 6.\,21.\,4$$

In the special case that both solutions are ideal (3) reduces to

$$\frac{m_s^\beta}{m_s^\alpha} = l_s^{\alpha\beta} \qquad\qquad 6.\,21.\,5$$

which is known as *Nernst's distribution law*.

§ 6. 22 SOLUBILITY OF PURE SOLID

For the equilibrium with respect to the species s between a solution and the pure solid phase we have the condition

$$\lambda_s = \lambda_s^S \qquad\qquad 6.\,22.\,1$$

where the superscript S denotes the pure solid phase. Substituting from (6. 11. 4) into (1) we obtain

$$m_s \gamma_s = \lambda_s^S/\lambda_s^\ominus \qquad \text{(saturated solution)} \qquad 6.\,22.\,2$$

From (2) we see that if several solutions in the same solvent at the same temperature are all saturated with the same solid phase of the species s, then in all these solutions $m_s \gamma_s$ has the same value.

Taking logarithms of (2), differentiating with respect to T and using (6. 05. 4) we obtain

$$\frac{\partial \ln m_s \gamma_s}{\partial T} = \frac{H_s^\infty - H_s^S}{RT^2} \qquad \text{(saturated solution)} \qquad 6.\,22.\,3$$

and we observe that the quantity $H_s^\infty - H_s^S$ occurring as the denominator on the right is the *molar heat of dissolution* of s at infinite dilution.

§ 6. 23 EXPERIMENTAL DETERMINATION OF φ

The most accurate direct method of determining φ experimentally is by measurements of freezing point and use of formula (6. 19. 12), which for a single solute species reduces to

$$\varphi m_s = \frac{[\Delta_f H_1^0]}{RT^0 TM_1}(T^0 - T) \qquad 6.\,23.\,1$$

All the quantities m_s, $\Delta_f H_1^0$, T^0, T can be measured and substitution of their values into (1) leads to experimental values of φ at the freezing point.

Let us suppose that freezing point measurements have been made so as to determine φ over a range of steadily decreasing values of m and let us consider what results are to be expected.

Since we know that as $m \to 0$ so $\varphi \to 1$, we may reasonably expect that $\varphi - 1$ can be expressed as a series of integral powers of m, say

$$\varphi - 1 = Am + Bm^2 + \ldots \qquad 6.\,23.\,2$$

This is in fact the case for non-electrolytes and we may then hope to determine by a series of accurate freezing point measurements the coefficients in such a formula as (2) so as to obtain a good fit. Formula (2) is not applicable to solutions of electrolytes; these will be discussed in chapter 8.

Let us now consider what will happen if the measurements are extended down to gradually decreasing values of m. If the measurements are performed with sufficient care, we may expect to reach a range where all terms of (2) are negligible except the first. In this range $(\varphi - 1)/m$ has a constant value A and we may confidently and reasonably assume that this behaviour persists down to $m = 0$. Suppose however we tried to confirm this experimentally, let us examine what would happen.

We may reasonably assume that the experimental error in measuring $T^0 - T$ is at least roughly independent of m. Since, at low values of m, the value of $T_0 - T$ is itself roughly proportional to m, it follows that the fractional experimental error in φ is inversely proportional to m. Hence according to (2) the fractional error in $\varphi - 1$ will be inversely proportional to m^2. It is therefore clear that by proceeding to experiment at smaller values of m, we eventually reach a stage where the experiments tell us nothing new.

The most reliable procedure is then to carry the experiments down to values of m where one finds experimentally

$$\frac{\varphi - 1}{m} = A \qquad (A \text{ const.}) \qquad 6.23.3$$

and then assume that this simple law persists down to $m = 0$.

We may mention that for solutions of non-electrolytes the limiting law (3) has not merely an empirical basis, but also a theoretical one based on statistical mechanics.

§ 6. 24 DETERMINATION OF γ FROM φ

We recall Bjerrum's relation for a single solute species (6. 13. 3)

$$\frac{\partial \{(\varphi - 1)r\}}{\partial r} = r \frac{\partial \ln \gamma}{\partial r} \qquad 6.24.1$$

which we may also write as

$$\frac{\partial \{(\varphi - 1)m\}}{\partial m} = m \frac{\partial \ln \gamma}{\partial m} \qquad 6.24.2$$

or as

$$\mathrm{d} \ln \gamma = \frac{\partial \{(\varphi - 1)m\}}{\partial m} \frac{\mathrm{d}m}{m} \qquad (\text{const. } T) \qquad 6.24.3$$

Integrating (3) from 0 to m and observing that $\varphi - 1$ and $\ln \gamma$ tend to zero as m tends to zero, we obtain

$$\ln \gamma = \int_0^m \frac{\partial \{(\varphi - 1)m\}}{\partial m} \frac{\mathrm{d}m}{m} = \varphi - 1 + \int_0^m (\varphi - 1) \frac{\mathrm{d}m}{m} \qquad 6.24.4$$

If φ has been determined at all molalities from 0 to m, we see that by using (4) we can in principle calculate γ at a molality m, but caution is required so as to avoid spurious results. We saw in the previous section that with regard to the experimental determination of γ there are three ranges of m, arranged in order of decreasing m, with the following characteristics.

1. Large molalities, where φ can be measured and fitted to a more or less complicated formula.

2. Intermediate molalities, where φ can be fitted to the formula

$$\varphi - 1 = Am \qquad (A \text{ const.}) \qquad 6.24.5$$

3. Lowest molalities, where no useful information about φ can be obtained by direct experiment and we assume that (5) continues to hold.

In using (4) it is expedient to break the range of integration at some value m' of m in the range where (5) is found to hold. We accordingly rewrite (4) as

$$\ln \gamma = (\varphi - 1) + \int_0^{m'} (\varphi - 1) \frac{\mathrm{d}m}{m} + \int_{m'}^m (\varphi - 1) \frac{\mathrm{d}m}{m} \qquad 6.\,24.\,6$$

We evaluate the first integral as follows

$$\int_0^{m'} (\varphi - 1) \frac{\mathrm{d}m}{m} = \int_0^{m'} A\,\mathrm{d}m = Am' = \varphi' - 1 \qquad 6.\,24.\,7$$

where φ' denotes the value of φ at $m = m'$. Using (7) in (6) we obtain finally

$$\ln \gamma = (\varphi - 1) + (\varphi' - 1) + \int_{m'}^m (\varphi - 1)\,\mathrm{d}\ln m \qquad 6.\,24.\,8$$

and the second integral can be evaluated from the experimental values of φ, either by fitting these to a formula or graphically.

The important point emerging from this discussion is that we cannot calculate γ from experimental determinations of φ, for example by freezing point measurements, without making an assumption concerning φ at low values of m. Since such an assumption has to be made anyway, it is just as well to make it explicitly and so obtain a closed formula for γ as well as for φ in the range of small m. For solutions of non-electrolytes, with which we are here concerned, the usual and most reasonable assumption is formula (5). In chapter 8, when we study solutions of electrolytes, we shall meet a different situation.

§ 6. 25 VAPOUR PRESSURE OF SATURATED SOLUTION

Throughout this chapter and the previous one we have never yet considered any equilibrium involving more than two bulk phases, nor shall we do so in any detail. No new principles are involved and the methods already described are applicable. We shall confine ourselves to a single interesting example.

We consider the following problem. How does the vapour pressure

of the solvent vary with the temperature in a solution kept saturated with a single non-volatile solid? Using the subscripts $_1$ for the solvent, $_2$ for the solute and the superscripts ^{G} for the gas phase, ^{S} for the solid and none for the solution, we have for variations maintaining equilibrium

$$d \ln \lambda_1 = d \ln \lambda_1^G \qquad 6.\,25.\,1$$

$$d \ln \lambda_2 = d \ln \lambda_2^S \qquad 6.\,25.\,2$$

Expanding these, we have

$$-\frac{H_1}{RT^2}\,dT + D \ln \lambda_1 = -\frac{H_1^G}{RT^2}\,dT + d \ln p_1 \qquad 6.\,25.$$

$$-\frac{H_2}{RT^2}\,dT + D \ln \lambda_2 = -\frac{H_2^S}{RT^2}\,dT \qquad 6.\,25.\,4 \;\backslash$$

Using $\Delta_e H$ to denote a heat of evaporation from the solution and $\Delta_f H$ to denote a heat of fusion into the solution, we can write (3) and (4) as

$$d \ln p_1 = D \ln \lambda_1 + \frac{\Delta_e H_1}{RT^2}\,dT \qquad 6.\,25.\,5$$

$$D \ln \lambda_2 = \frac{\Delta_f H_2}{RT^2}\,dT \qquad 6.\,25.\,6$$

We now use the Gibbs-Duhem relation in the form

$$D \ln \lambda_1 + r\,D \ln \lambda_2 = 0 \qquad 6.\,25.\,7$$

to eliminate λ_1, λ_2 from (5), (6). We thus obtain

$$\frac{d \ln p_1}{dT} = \frac{1}{RT^2}\,(\Delta_e H_1 - r\Delta_f H_2) \qquad 6.\,25.\,8$$

It is interesting to observe that the expression inside the brackets is equal and opposite to the *heat of formation* of the quantity of solution containing one mole of solvent from the gaseous solvent and from the solid solute.

§ 6. 26 SURFACE TENSION

We conclude this chapter with a brief discussion of interfacial layers, particularly those between a liquid and its vapour.

As described in § 5. 53 we shall neglect effects of pressure on the

liquid phase and on the surface layer. We have then by analogy with (5. 53. 4), (5. 53. 5) and (5. 53. 6)

$$-\mathrm{d}\gamma = S^\sigma \, \mathrm{d}T + \Gamma_1 \, \mathrm{d}\mu_1 + \Sigma_s \, \Gamma_s \, \mathrm{d}\mu_s \qquad \text{6. 26. 1}$$

$$\mathrm{d}\mu_1 = -S_1\mathrm{d}T + \mathrm{D}\mu_1 \qquad \text{6. 26. 2}$$

$$\mathrm{d}\mu_s = -S_s\mathrm{d}T + \mathrm{D}\mu_s \qquad \text{6. 26. 3}$$

where (2) and (3) relate to the liquid phase *. We also have in the liquid phase the Gibbs-Duhem relation (6.06.1)

$$\mathrm{D}\mu_1 + \Sigma_s \, r_s \, \mathrm{D}\mu_s = 0 \qquad \text{6. 26. 4}$$

Substituting (2) and (3) into (1) we obtain

$$-\mathrm{d}\gamma = (S^\sigma - \Gamma_1 S_1 - \Sigma_s \, \Gamma_s S_s) \, \mathrm{d}T + \Gamma_1 \, \mathrm{D}\mu_1 + \Sigma_s \, \Gamma_s \, \mathrm{D}\mu_s \qquad \text{6. 26. 5}$$

Now eliminating $\mathrm{D}\mu_1$ between (4) and (5) we obtain finally

$$-\mathrm{d}\gamma = (S^\sigma - \Gamma_1 S_1 - \Sigma_s \, \Gamma_s S_s) \, \mathrm{d}T + \Sigma_s \, (\Gamma_s - r_s \Gamma_1) \, \mathrm{D}\mu_s \qquad \text{6. 26. 6}$$

By reasoning similar to that of § 5. 54 one can verify the invariance of the coefficients of $\mathrm{d}T$ and $\mathrm{D}\mu_s$ with respect to shifts of the geometrical surfaces bounding the surface layer.

§ 6. 27 TEMPERATURE DEPENDENCE

For the temperature dependence of the surface tension at constant composition of the liquid, that is $\mathrm{D}\mu_s = 0$ (all s), we obtain immediately from (6. 26. 6)

$$-\frac{\mathrm{d}\gamma}{\mathrm{d}T} = S^\sigma - \Gamma_1 S_1 - \Sigma_s \, \Gamma_s S_s \qquad \text{6. 27. 1}$$

where the right side is the entropy of unit area of the surface layer less the entropy of the same material content in the liquid phase.

By proceeding as in § 5. 55 we can transform (1) to the equivalent relation

$$\gamma - T\frac{\mathrm{d}\gamma}{\mathrm{d}T} = U^\sigma - \Gamma_1 U_1 - \Sigma_s \, \Gamma_s U_s \qquad \text{6. 27. 2}$$

where the right side is the energy which must be supplied, partly as

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* There should be no confusion between γ denoting surface tension and the activity coefficients γ_s.

work and partly as heat, to prevent any change of temperature when unit area of surface is formed from the liquid.

§ 6. 28 VARIATIONS OF COMPOSITION

For variations of composition at constant temperature (6. 26. 6) reduces to

$$-\mathrm{d}\gamma = \Sigma_s \left(\Gamma_s - r_s \Gamma_1 \right) \mathrm{D}\mu_s \qquad \text{6. 28. 1}$$

or using

$$\mathrm{D}\mu_s = RT \, \mathrm{D} \ln \lambda_s \qquad \text{6. 28. 2}$$

$$-\mathrm{d}\gamma = RT \, \Sigma_s \left(\Gamma_s - r_s \Gamma_1 \right) \mathrm{D} \ln \lambda_s \qquad \text{6. 28. 3}$$

Each of the quantities

$$\Gamma_s - r_s \Gamma_1 \qquad \text{6. 28. 4}$$

occurring on the right side of (3) may be called the *surface excess per unit area* of the solute species s. The corresponding quantity for the solvent species 1 vanishes by definition. As we have repeatedly stressed, each quantity (4), in contrast to the individual Γ_s, is invariant with respect to shift of the boundary between the liquid phase and the surface phase and is therefore physically significant. The quantities (4) are the same as the quantities which Gibbs * denoted by $\Gamma_{s(1)}$, but his definition of these quantities was more abstract and more difficult to visualize.

§ 6. 29 INTERFACIAL TENSION BETWEEN TWO SOLUTIONS

For the interface between two liquid phases a, β neglecting dependence on pressure, we have

$$-\mathrm{d}\gamma = S^\sigma \mathrm{d}T + \Gamma_1 \mathrm{d}\mu_1 + \Sigma_s \, \Gamma_s \, \mathrm{d}\mu_s \qquad \text{6. 29. 1}$$

The Gibbs-Duhem relation for phase a can be written

$$\left(1 + \Sigma_s r_s^a \right) S_m^a \, \mathrm{d}T + \mathrm{d}\mu_1 + \Sigma_s r_s^a \, \mathrm{d}\mu_s = 0 \qquad \text{6. 29. 2}$$

and that for phase β

$$\left(1 + \Sigma_s r_s^\beta \right) S_m^\beta \, \mathrm{d}T + \mathrm{d}\mu_1 + \Sigma_s r_s^\beta \, \mathrm{d}\mu_s = 0 \qquad \text{6. 29. 3}$$

If there are $c - 1$ solute species, there are $c + 1$ quantities $\mathrm{d}T$, $\mathrm{d}\mu_1$, $\mathrm{d}\mu_s$ in (1) of which any two can be eliminated by using (2) and (3). The results obtainable are complicated and we shall not pursue them here.

* Gibbs, *Collected Works*, vol. 1 pp. 234—235.

§ 6. 30 VOLUME CONCENTRATIONS

In analytical work it has long been the usual practice to describe the composition of a solution by the *volume concentration* c_s of each solute species defined as

$$c_s = \frac{n_s}{V} = r_s \frac{n_1}{V} = m_s \frac{n_1 M_1}{V} \qquad 6.\,30.\,1$$

·As long as one is concerned with the properties of the solution at only one temperature this practice is unobjectionable. But in thermodynamics we are much interested in the temperature dependence of properties, and volume concentrations are then inconvenient. For whatever quantities be used to describe the composition of a liquid solution, it is expedient to use as the other two independent variables temperature and pressure, so that differentiation with respect to temperature implies constant pressure. We therefore have

$$\frac{\partial c_s}{\partial T} = -a c_s \qquad 6.\,30.\,2$$

where a is the coefficient of thermal expansion. It is evident from (2) that, if c_s is chosen as a variable, it will not be an independent variable. On these grounds volume concentrations are not convenient in liquid solutions and we shall not use them.

Volume concentrations of course play an important part in the theory of gas kinetics. The implication, sometimes met, that they must therefore play a parallel part in the theory of solution kinetics shows a lack of appreciation of the utterly different and much more complex meaning of the word *collision* * applied to a solution in contrast to a gas.

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* We have not yet a complete theoretical treatment of collisions in solution, but the author believes that a successful theory would be based on molecular ratios rather than on volume concentrations.

SYSTEMS OF CHEMICALLY REACTING SPECIES

§ 7. 01 NOTATION AND TERMINOLOGY

We recall the notation introduced in § 1. 49 and § 1. 50 which we shall continue to use. We write

$$\Sigma \nu_A A \to \Sigma \nu_B B \qquad 7.\,01.\,1$$

meaning that at constant temperature ν_A moles of A in a well defined state and the like react to form ν_B moles of B in a well defined state and the like. In § 1. 49 we gave examples to illustrate the meaning of A, B and of ν_A, ν_B. The coefficients ν_A, ν_B are always either small integers or simple rational fractions.

We stress the importance, before discussing any specific equilibrium, of writing down explicitly the formula of type (1) about which we are talking. For example to state that some constant describing the equilibrium between hydrogen and oxygen has a specified value is completely meaningless unless one states which of the following formulae one has in mind:

$$2H_2 + O_2 \to 2H_2O$$
$$H_2 + \tfrac{1}{2}O_2 \to H_2O$$
$$2H_2O \to 2H_2 + O_2$$
$$H_2O \to H_2 + \tfrac{1}{2}O_2$$
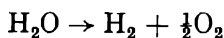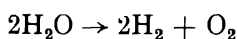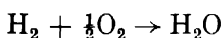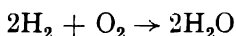
The constants corresponding to these four alternative formulae will all be different, but of course interrelated. It is also important to specify the state of each reacting species, e.g. H_2O (g) or H_2O (l), unless it is obvious as in the case of H_2 at ordinary temperatures which can only be H_2 (g).

We can measure the extent to which the process (1) takes place by the *extent of reaction* defined in § 1. 50, such that a change of ξ to $\xi + d\xi$ means that $\nu_A\, d\xi$ moles of A and the like react to give $\nu_B\, d\xi$ moles of B and the like. We also recall that the affinity A of the process (1) is formally defined by

$$A = -\left(\frac{\partial F}{\partial \xi}\right)_{T,\,V^u} = -\left(\frac{\partial G}{\partial \xi}\right)_{T,\,P^a} \qquad 7.\,01.\,2$$

where V^a denotes the volume of each phase a and P^a the pressure of each phase a.

We then have the concise universal rule that in any natural process

$$A\,d\xi > 0 \qquad\qquad \text{(natural)} \qquad\qquad 7.\,01.\,3$$

and consequently for equilibrium

$$A = 0 \qquad\qquad \text{(equilibrium)} \qquad\qquad 7.\,01.\,4$$

This equation is a concise method of stating that

$$\Sigma\,\nu_A\mu_A = \Sigma\,\nu_B\mu_B \qquad \text{(equilibrium)} \qquad\qquad 7.\,01.\,5$$

This completes our recapitulation of the most important formulae of § 1. 49 and § 1. 50. We now recall the definition in (4. 15. 2) of absolute activities λ

$$\mu = RT \ln \lambda \qquad\qquad 7.\,01.\,6$$

according to which (5) can be transcribed to

$$\frac{\Pi\,(\lambda_B)^{\nu_B}}{\Pi\,(\lambda_A)^{\nu_A}} = 1 \qquad \text{(equilibrium)} \qquad\qquad 7.\,01.\,7$$

We now introduce a new notation, leading to considerable condensation, of which we shall make much use.

Let I_A denote any intensive function relating to the species A, such as for example λ_A, p_A, x_A, γ_A and similarly for I_B. Then we use the contracted notation $\Pi\,(I)$ defined by

$$\Pi\,(I) \equiv \frac{\Pi\,(I_B)^{\nu_B}}{\Pi\,(I_A)^{\nu_A}} \qquad\qquad 7.\,01.\,8$$

When in particular the I's have values corresponding to a state of chemical equilibrium, we shall call $\Pi\,(I)$ the *equilibrium* quotient of the I's.

Our first application of this notation is to (7), which we contract to

$$\Pi\,(\lambda) = 1 \qquad\qquad \text{(equilibrium)} \qquad\qquad 7.\,01.\,9$$

and the general condition for chemical equilibrium can be stated in the form: *the equilibrium quotient of the absolute activities* is unity.

§ 7. 02 HEATS OF REACTION

Consider the process

$$\Sigma\,\nu_A\,A \to \Sigma\,\nu_B\,B \qquad\qquad 7.\,02.\,1$$

and let the operator Δ denote the excess of a final over an initial value

corresponding to unit increase in the extent of reaction, the temperature remaining constant throughout.

If the process occurs at constant pressure then the heat absorbed is equal to ΔH. For this reason ΔH is called the *heat of reaction at constant pressure* or sometimes just the *heat of reaction*.

If on the other hand the process occurs at constant volume the heat absorbed is equal to ΔU, which is therefore called the *heat of reaction at constant volume*. This quantity is of little importance except for gas reactions, for which it is related to ΔH by

$$\Delta U = \Delta H - RT \, \Delta \Sigma \nu \qquad 7.\,02.\,2$$

neglecting terms involving the second virial coefficients.

We recall that for a perfect gas H is independent of the pressure and for a condensed phase the effect of variations of pressure is negligible. It is therefore usually unnecessary to specify the pressure when speaking of heats of reaction.

§ 7. 03 HESS' LAW

Since H is a function of the state of a system, ΔH is for successive processes at the same temperature an additive function. This property of ΔH, known as *Hess' law*, is useful in enabling us to calculate ΔH for a reaction, difficult to produce quantitatively, from other reactions which give less difficulty. The following simple example will illustrate the point

$$C \text{ (graphite)} + O_2 \text{ (g)} \rightarrow CO_2 \text{ (g)} \qquad -\Delta H = 393.5 \text{ kJ}$$

$$CO \text{ (g)} + \tfrac{1}{2}O_2 \text{ (g)} \rightarrow CO_2 \text{ (g)} \qquad -\Delta H = 283.0 \text{ kJ}$$
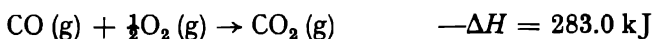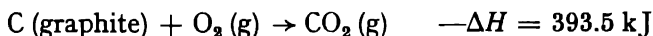
In both the above cases ΔH is readily measurable. By subtraction we obtain

$$C \text{ (graphite)} + \tfrac{1}{2}O_2 \text{ (g)} \rightarrow CO \text{ (g)} \qquad -\Delta H = 110.5 \text{ kJ}$$

a reaction difficult, if not impossible to study quantitatively.

Other numerous examples are the calculations of the *heats of formation* of organic compounds from the directly measured *heats of combustion*. A simple example is

$$CH_4 \text{ (g)} + 2O_2 \text{ (g)} \rightarrow CO_2 \text{ (g)} + 2H_2O \text{ (l)} \qquad -\Delta H = 890.3 \text{ kJ}$$

$$C \text{ (graphite)} + O_2 \text{ (g)} \rightarrow CO_2 \text{ (g)} \qquad -\Delta H = 393.5 \text{ kJ}$$

$$2H_2 \text{ (g)} + O_2 \text{ (g)} \rightarrow 2H_2O \text{ (l)} \qquad -\Delta H = 571.6 \text{ kJ}$$
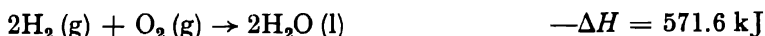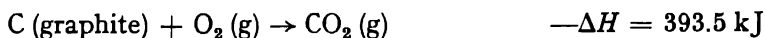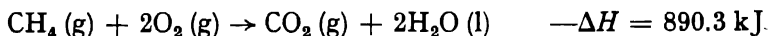
from which we immediately deduce

C (graphite) $+ 2H_2$ (g) $\rightarrow CH_4$ (g) $-\Delta H = 74.8$ kJ
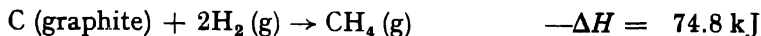
Unfortunately in calculating a heat of formation as the difference between much greater heats of combustion, since the experimental errors add up, there is considerable loss in percentage accuracy. Nevertheless this is the standard method for determining heats of formation of organic compounds from their elements.

Unfortunately some authors have used the name *heat of reaction* for $-\Delta H$ instead of for ΔH. This practice is deplorable. The simplest and safest way to avoid any possible ambiguity is to write in full $\Delta H = \ldots$ or $-\Delta H = \ldots$ as in the above examples.

§ 7. 04 KIRCHHOFF'S RELATIONS

We often need the value of ΔH at one temperature when it has been measured at a different temperature. This causes no difficulty provided the dependence of H on the temperature has been measured or is known theoretically for the initial and final states.

Let T denote the temperature at which we want the value of ΔH and T' the temperature at which is has been measured. Then

$$\Delta H(T) - \Delta H(T')$$
$$= \{\Sigma \nu_B H_B(T) - \Sigma \nu_A H_A(T)\} - \{\Sigma \nu_B H_B(T') - \Sigma \nu_A H_A(T')\}$$
$$= \Sigma \nu_B \{H_B(T) - H_B(T')\} - \Sigma \nu_A \{H_A(T) - H_A(T')\} \qquad 7.04.1$$

Although (1) is the form in which the experimental data are available and should be used, it is customary to express (1) in the differential form

$$\frac{d}{dT}\Delta H = \Delta \frac{dH}{dT} = \Sigma \nu_B \frac{dH_B}{dT} - \Sigma \nu_A \frac{dH_A}{dT}$$

$$= \Sigma \nu_B C_B - \Sigma \nu_A C_A \qquad 7.04.2$$

Formula (2) is known as *Kirchhoff's relation*. Since values of the heat capacities C are usually obtained by differentiating experimental measurements of $H(T) - H(T')$ and formula (2), if used, has to be integrated, it is difficult to see any advantage of (2) over (1). As already mentioned in § 4. 05 the main function of a heat capacity is to serve as the connecting link between the heat function and the entropy.

There is a second formula also associated with Kirchhoff, similar to (2), but relating the energy change ΔU with the heat capacities at constant volume, but this formula is not needed.

§ 7. 05 GASEOUS EQUILIBRIA

In studying gaseous equilibria we shall treat all gases as perfect. When this is not justifiable, it is only necessary to correct by replacing partial pressures by fugacities. As a matter of fact there are scarcely any experimental data on gaseous equilibria of sufficient accuracy for the distinction to be significant. In any case the lack of experimental data on second virial coefficients in gaseous mixtures makes it impossible to apply the correction in practice, even though the method is in principle straightforward.

We accordingly use formula (5. 17. 3)

$$\lambda_i = \lambda_i^\dagger \frac{p_i}{P^\dagger} \qquad 7.\,05.\,1$$

where we recall that $P^\dagger$ denotes an arbitrarily chosen standard pressure, usually one atmosphere, and $\lambda_i^\dagger$ denotes the value of λ_i for the pure single gas at this standard pressure. Thus $\lambda_i^\dagger$ is a function of temperature only. Substituting (1) into (7. 01. 9), we obtain as equilibrium condition

$$\Pi\,(p) = K(T) \qquad 7.\,05.\,2$$

where $K(T)$ is a function of temperature only defined by

$$K = \Pi\,(P^\dagger/\lambda^\dagger) \qquad 7.\,05.\,3$$

and is called the *equilibrium constant*.

§ 7. 06 ENERGY AND ENTROPY CONSTANTS

The correctness of the formulae of § 7. 05 requires that the arbitrary conventions concerning zero energy and zero entropy, inasmuch as these affect the values of the $\lambda^\dagger$'s, must be the same for all the reacting species. We shall now investigate this important point.

Referring back to (4. 29. 1) we assume for a gas with *monatomic molecules*

$$\lambda^\dagger = e^{H^0/RT} \left(\frac{\Theta^\dagger}{T}\right)^{\frac{5}{2}} \qquad 7.\,06.\,1$$

In §§ 4. 30—4. 33 we saw that for diatomic and polyatomic molecules $\lambda^\dagger$ contains the factor on the right of (1) as well as other factors completely determined by the rotational and other internal degrees of freedom of the molecules.

Correspondingly all formulae contain a term H^0 in the molar heat function and a term $-\frac{5}{2}R \ln \Theta^\dagger$ in the molar entropy. As long as we are considering only variations of temperature, pressure and mixing of gases these terms may be regarded as arbitrary constants without physical significance. It is only when a gas changes into something else that we need to watch how these constants come in.

We have already in § 4. 55 considered the bearing of these constants on equilibrium between gas and crystal. As regards H^0 all that was required was that the arbitrary constant in the molar energies and heat functions of the gas and crystal should be adjusted so as to correspond to the same scale. The same requirement obviously holds for gases which can be changed into one another by chemical reactions. In other words the values assigned to H^0 for any one gas or for several gases which cannot be changed into one another are entirely arbitrary. But for gases which can be changed into one another the values assigned to H^0_A, H^0_B must be mutually adjusted so that at some one temperature the value then calculated for the heat of reaction $\Sigma \nu_B H_B - \Sigma \nu_A H_A$ agrees with the experimental value. When this adjustment has been made at one temperature, the convention is automatically consistent for all temperatures.

The most used convention is to adjust H^0 for every *element* so that H_m has the value zero for the element in its most stable state at 25 °C or 298.15 °K. The value of H^0 for any compound must then be adjusted so that the value of H_m at 298.15 °K is equal to ΔH for the formation of the compound from its elements. Values of H_m at 298.15 °K have been tabulated for the commonest compounds. In order to fix these values it is not necessary nor usually possible to have a direct measurement of the heat of formation, but the values are calculated from measurements of other heats of reaction by using Hess' law as described in § 7. 03. Nor is it necessary that all the measurements used should have been made at 298.15 °K nor even all at the same temperature, for they can be corrected from one temperature to another as described in § 7. 04.

We turn now to the term $-\frac{3}{2}R \ln \Theta^\dagger$ in the molar entropy. In § 4. 56 and § 4. 59 we gave an explicit formula for $\Theta^\dagger$ according to a conventional, but completely specified, choice of states of zero entropy for each substance. Statistical theory tells us that when this same convention is applied to every substance, the entropy scales of all substances are mutually consistent. The experimental verification of this is that equilibria calculated from the formulae of § 4. 56 and § 4. 59

are in fact in good agreement with experiment. We shall give a specific numerical example in § 7. 10.

Formulae (7. 05. 2) and (7. 05. 3) express the equilibrium quotient of the partial pressures p in terms of the $\lambda^\dagger$. We have expressed these relations in a form independent of any particular choice of the standard pressure $P^\dagger$. As we can see from formula (4. 56. 3) the choice of $P^\dagger$ affects the value of $\lambda^\dagger$ through $\Theta^\dagger$.

The formulae of § 5.17 for a binary perfect gas can immediately be generalized for a perfect gas of any number of components. In particular we have for each component i

$$\lambda_i = \lambda_i^\dagger \, p_i/P^\dagger \qquad\qquad 7.07.1$$

$$\mu_i = \mu_i^\dagger + RT \ln \frac{p_i}{P^\dagger} \qquad\qquad 7.07.2$$

$$S_i = -\frac{\mathrm{d}\mu_i^\dagger}{\mathrm{d}T} - R \ln \frac{p_i}{P^\dagger} \qquad\qquad 7.07.3$$

$$H_i = \mu_i^\dagger - T \frac{\mathrm{d}\mu_i^\dagger}{\mathrm{d}T} \qquad\qquad 7.07.4$$

$$\mu_i^\dagger = RT \ln \lambda_i^\dagger \qquad\qquad 7.07.5$$

It is evident that the values of the *standard absolute activity* $\lambda_i^\dagger$, of the *standard chemical potential* $\mu_i^\dagger$ and of the *standard molar entropy* $-\mathrm{d}\mu_i^\dagger/\mathrm{d}T$ all depend on the choice of the *standard pressure* $P^\dagger$. Usually $P^\dagger$ is taken to be one atmosphere, but not always. Whenever a numerical value of a standard property is quoted it is therefore essential to specify the choice of $P^\dagger$.

A simpler, but less usual, procedure is not to use the word standard at all but to speak of, for example, the *molar entropy at one atmosphere*, or more briefly the *atmospheric molar entropy*. This terminology avoids any possibility of ambiguity.

We shall in fact always take $P^\dagger$ to be one atmosphere. It is hardly necessary to remark that this choice does not compel us to use the

atmosphere as our unit of pressure. We accordingly have the relations

$$S_i = S_i^{\ddagger} - R \ln \frac{p_i}{\text{atm}}$$

$$= S_i^{\ddagger} - R \ln \frac{p_i}{760 \text{ mm Hg}}$$

$$= S_i^{\ddagger} - R \ln \frac{p_i}{1.013 \times 10^6 \text{ erg cm}^{-3}} \qquad 7.\,07.\,6$$

where $S_i^{\ddagger} = -d\mu_i^{\ddagger}/dT$ is the molar entropy at one atmosphere.

All accurate calorimetric work measures energy in joules and so entropy in J deg^{-1} and molar entropies in J deg^{-1} mole^{-1}. Sometimes considerable effort is wasted in converting these values into cal deg^{-1} mole^{-1}. No objection is raised to this, but some authors who adopt this procedure call this unit the *entropy unit*. The statement that a certain entropy is 1.2 entropy units is just as silly as stating that a certain pressure is 1.2 *pressure units*.

Actually it is extremely convenient, especially in theoretical work to give and use numerical values of S_m/R which is dimensionless.

§ 7. 08 OTHER EQUILIBRIUM CONSTANTS

We recall that we obtained the condition for equilibrium in a gaseous reaction in the form (7. 05. 2)

$$\Pi\,(p) = K \qquad 7.\,08.\,1$$

where K is a function of temperature only. By using the perfect gas equation of state in the form

$$p = RTc \qquad 7.\,08.\,2$$

where c denotes the concentration n/V, we can transform (1) to

$$\Pi\,(c) = K_c \qquad 7.\,08.\,3$$

where

$$K_c = K\,(RT)^{-\Delta\Sigma\nu} \qquad 7.\,08.\,4$$

Again by using the definition of partial pressure

$$p = xP \qquad 7.\,08.\,5$$

we can transform (1) to

$$\Pi\,(x) = KP^{-\Delta\Sigma\nu} \qquad\qquad 7.\,08.\,6$$

We observe that, whereas $\Pi(p) = K$ and $\Pi(c) = K_c$ depend only on the temperature, $\Pi(x)$ also depends on the pressure except when $\Sigma\nu_A = \Sigma\nu_B$.

We have quoted (3) and (6) for the sake of completeness, but as they merely state the same as (1) in a different way, they are unnecessary.

§ 7. 09 TEMPERATURE COEFFICIENT

We recall that for a perfect gas according to (5. 17. 12)

$$H_i = -RT^2 \frac{\mathrm{d}\ln\lambda_i^\dagger}{\mathrm{d}T} \qquad\qquad 7.\,09.\,1$$

Taking logarithms of (7. 05. 3) and writing it in full we have

$$\ln K = \Sigma\,\nu_A \ln \frac{\lambda_A^\dagger}{P^\dagger} - \Sigma\,\nu_B \ln \frac{\lambda_B^\dagger}{P^\dagger} \qquad\qquad 7.\,09.\,2$$

Differentiating (2) with respect to T and substituting from (1), we obtain

$$\frac{\mathrm{d}\ln K}{\mathrm{d}T} = \frac{\Sigma\,\nu_B H_B - \Sigma\,\nu_A H_A}{RT^2} = \frac{\Delta H}{RT^2} \qquad\qquad 7.\,09.\,3$$

where ΔH denotes the *heat of reaction*.

By differentiating (7. 08. 4) with respect to T and comparing with (3) we find

$$\frac{\mathrm{d}\ln K_c}{\mathrm{d}T} = \frac{\mathrm{d}\ln K}{\mathrm{d}T} - \frac{\Sigma\,\nu_B - \Sigma\,\nu_A}{T}$$

$$= \frac{\Delta H - (\Sigma\,\nu_B - \Sigma\,\nu_A)\,RT}{RT^2} = \frac{\Delta U}{RT^2} \qquad\qquad 7.\,09.\,4$$

a relation due to van 't Hoff.

§ 7.10 WATER-GAS REACTION

We shall now give an example of the detailed calculation of a gaseous equilibrium constant, choosing the water-gas reaction at 1000 °K

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (T = 1000 \text{ °K})$$
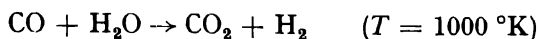
According to (7.05. 3), we have

$$K = \frac{\lambda_{CO}^{\dagger} \, \lambda_{H_2O}^{\dagger}}{\lambda_{CO_2}^{\dagger} \, \lambda_{H_2}^{\dagger}} \qquad\qquad 7.10.1$$

or taking logarithms

$$\ln K = -\ln \lambda_{CO_2}^{\dagger} - \ln \lambda_{H_2}^{\dagger} + \ln \lambda_{CO}^{\dagger} + \ln \lambda_{H_2O}^{\dagger} \qquad 7.10.2$$

We rewrite this in the form

$$\begin{aligned}
\ln K &= (-\ln \lambda_{CO_2}^{\dagger} + H_{CO_2}^0/RT) \\
&\quad + (-\ln \lambda_{H_2}^{\dagger} + H_{H_2}^0/RT) \\
&\quad - (-\ln \lambda_{CO}^{\dagger} + H_{CO}^0/RT) \\
&\quad - (-\ln \lambda_{H_2O}^{\dagger} + H_{H_2O}^0/RT) \\
&\quad + \left(\frac{H_{CO}^0 + H_{H_2O}^0 - H_{CO_2}^0 - H_{H_2}^0}{RT}\right) \qquad 7.10.3
\end{aligned}$$

and we compute separately each of the quantities in brackets.

We begin with the last. The heat of reaction at 25 °C is given by [*]

$$-\Delta H = 9.83_8 \text{ kcal} = 41.16 \text{ kJ} \qquad (T = 298.15 \text{ °K}) \quad 7.10.4$$

This is the only piece of experimental thermodynamic or calorimetric data which we shall need to use. For the sake of brevity, let us denote the temperature 298.15 °K by T'. We have then

$$-\frac{\Delta H(T')}{R} = \frac{41160}{8.3147} \text{ deg} = 4950 \text{ deg} \qquad 7.10.5$$

We write down the identity

$$\begin{aligned}
-\Delta H(T') &= H_{CO}(T') + H_{H_2O}(T') - H_{CO_2}(T') - H_{H_2}(T') \\
&= -\Delta H^0 + \{H_{CO}(T') - H_{CO}^0\} + \{H_{H_2O}(T') - H_{H_2O}^0\} \\
&\quad - \{H_{CO_2}(T') - H_{CO_2}^0\} - \{H_{H_2}(T') - H_{H_2}^0\} \qquad 7.10.6
\end{aligned}$$

where ΔH^0 is defined by

$$\Delta H^0 = H_{CO_2}^0 + H_{H_2}^0 - H_{CO}^0 - H_{H_2O}^0 \qquad 7.10.7$$

[*] Rossini and others, *Bur. Stand. J. Res., Wash.* 1945 **34** 143.

We now use formula (4. 31. 4), neglecting the terms containing the second virial coefficient B, and the spectroscopic data in table 4. 3 to calculate

$$\{H_{CO_2}(T') - H^0_{CO_2}\}/R = 1126 \text{ deg} \qquad 7.\,10.\,8$$

We similarly use formula (4. 30. 10) and the data in table 4. 2 to calculate

$$\{H_{H_2}(T') - H^0_{H_2}\}/R = 1044 \text{ deg} \qquad 7.\,10.\,9$$

$$\{H_{CO}(T') - H^0_{CO}\}/R = 1044 \text{ deg} \qquad 7.\,10.\,10$$

Similarly using (4. 32. 5) and the data in table 4. 4, we find

$$\{H_{H_2O}(T') - H^0_{H_2O}\}/R = 1194 \text{ deg} \qquad 7.\,10.\,11$$

Substituting (5), (8), (9), (10), (11) into (6) we obtain

$$-\Delta H^0/R = \{4950 + 1126 + 1044 - 1044 - 1194\} \text{ deg}$$
$$= 4882 \text{ deg} \qquad 7.\,10.\,12$$

Consequently at 1000 °K the last bracket of (3) has the value

$$\frac{\Delta H^0}{RT} = 4.88_3 \qquad (T = 1000 \text{ °K}) \qquad 7.\,10.\,13$$

We turn now to the computation of the other four brackets on the right of (3). Each of these is the sum of the following three contributions:

(a)   the terms given by formula (4. 58. 2) for monatomic molecules, which we shall call the *particle contribution*, since they do not include contributions from internal degrees of freedom;

(b)   the contributions of the rotational degrees of freedom;

(c)   the contributions of the internal vibrations.

The particle contribution is given directly by (4. 58. 2).

The rotational contributions to $\ln \lambda^\dagger$ are, as described in §§ 4. 30—4. 32, given for the symmetrical linear molecules CO_2 and H_2 by

$$-\ln \frac{T}{2\Theta_r} \qquad 7.\,10.\,14$$

for the unsymmetrical linear molecule CO by

$$-\ln \frac{T}{\Theta_r} \qquad 7.\,10.\,15$$

and for the non-linear molecule H_2O by formula (4. 32. 1). The values of Θ_r are given in tables 4. 2, 4. 3 and 4. 4.

The contribution of each vibrational degree of freedom to $\ln \lambda^{\dagger}$ according to (4. 30. 5) is

$$\ln (1 - e^{-\Theta_v/T}) \qquad \text{7. 10. 16}$$

and the values of Θ_v are given in tables 4. 2, 4. 3 and 4. 4.

The results of these computations are given in table 7. 1. Inserting these and (13) into (3), we obtain

$$\ln K = 27.220 + 16.430 - 24.550 - 23.669 + 4.882$$
$$= 0.313 \qquad \text{7. 10. 17}$$

so that $K = 1.37$ in satisfactory agreement with experiment [*].

TABLE 7. 1

Contributions to $- \log \lambda^{\dagger} + H^0/RT$

	CO_2	H_2	CO	H_2O
Particle	19 28$_1$	14 65$_5$	18.60$_3$	17.94$_1$
Rotation	6 79$_4$	1.77$_2$	5.90$_0$	5 61$_1$
Vibration	1 14$_5$	0 00$_3$	0.04$_7$	0.11$_7$
Resultant	27 22$_0$	16 43$_0$	24 55$_0$	23 66$_9$

§ 7. 11 EQUILIBRIA BETWEEN GASES AND SOLIDS

We turn now to a discussion of the equilibrium of reactions involving pure solids as well as gases. Examples are

$$CaCO_3 \text{ (s)} \rightarrow CaO \text{ (s)} + CO_2 \text{ (g)} \qquad \text{7. 11. 1}$$

$$NH_4Cl \text{ (s)} \rightarrow NH_3 \text{ (g)} + HCl \text{ (g)} \qquad \text{7. 11. 2}$$

$$C \text{ (graphite)} + CO_2 \text{ (g)} \rightarrow 2CO \text{ (g)} \qquad \text{7. 11. 3}$$
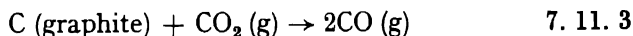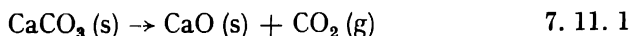
We have the general equilibrium condition (7. 01. 9)

$$\Pi (\lambda) = 1 \qquad \text{7. 11. 4}$$

where the λ of each gaseous species is related to its partial pressure p by (7. 05. 1). On the other hand we may regard the λ of each pure solid

[*] For detailed references to experimental data, see Bryant, *Industr. Engng. Chem.* 1931 **23** 1019.

as a function of temperature only, since the effect of change of pressure on a solid is usually negligible.

We now extend our Π notation as follows. We write

$$\Pi\,(I) = \Pi_G\,(I)\,\Pi_S\,(I) \qquad\qquad 7.\,11.\,5$$

where $\Pi_G\,(I)$ contains all the factors of $\Pi\,(I)$ relating to the gaseous species and $\Pi_S\,(I)$ all the factors relating to the solid species.

For example in the case of reaction (1)

$$\Pi_G\,(\lambda) = \lambda_{CO_2} \qquad\qquad 7.\,11.\,6$$

$$\Pi_S\,(\lambda) = \frac{\lambda_{CaO}}{\lambda_{CaCO_3}} \qquad\qquad 7.\,11.\,7$$

Using this notation, the equilibrium condition (4) may be written

$$\Pi_G\,(\lambda)\,\Pi_S\,(\lambda) = 1 \qquad\qquad 7.\,11.\,8$$

Now substituting (7. 05. 1) into (8), we obtain

$$\Pi_G\,(p) = K \qquad\qquad 7.\,11.\,9$$

where K is a function of temperature only given by

$$K = \Pi_G\,(P^\dagger/\lambda^\dagger)/\Pi_S\,(\lambda) \qquad\qquad 7.\,11.\,10$$

and is called the *equilibrium constant*. For example for reaction (3), we have

$$\frac{p_{CO}^2}{p_{CO_2}} = K \qquad\qquad 7.\,11.\,11$$

$$K = \frac{\lambda_{CO_2}^\dagger\,\lambda_C\,P^\dagger}{\lambda_{CO}^{\dagger 2}} \qquad\qquad 7.\,11.\,12$$

§ 7. 12 TEMPERATURE COEFFICIENT

For each gaseous species G, we have

$$\frac{d\ln\lambda_G^\dagger}{dT} = -\,\frac{H_G}{RT^2} \qquad\qquad 7.\,12.\,1$$

and for each solid species S

$$\frac{d\ln\lambda_S}{dT} = -\,\frac{H_S}{RT^2} \qquad\qquad 7\,12.\,2$$

Taking logarithms of (7. 11. 10), differentiating with respect to T and substituting (1) and (2), we obtain

$$\frac{d \ln K}{dT} = \frac{\Sigma \nu_B H_B - \Sigma \nu_A H_A}{RT^2} = \frac{\Delta H}{RT^2} \qquad 7.\ 12.\ 3$$

where ΔH denotes the *heat of reaction*. It will be seen that (3) has the same form as formula (7. 09. 3) for a gaseous reaction.

§ 7. 13 NUMERICAL EXAMPLE

We shall illustrate the use of the formulae of § 7. 11 by a specific example and we choose the reaction

$$C\ (\text{graphite}) + CO_2\ (g) \rightarrow 2CO\ (g) \qquad 7.\ 13.\ 1$$
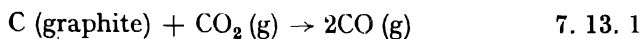
The equilibrium is determined by

$$\frac{p^2_{CO}}{p_{CO_2}} = K \qquad 7.\ 13.\ 2$$

where

$$K = \frac{\lambda^{\dagger}_{CO_2}\, \lambda_C}{\lambda^{\dagger 2}_{CO}}\ \text{atm} \qquad 7.\ 13.\ 3$$

We shall evaluate K at 1000 °K.

In analogy with (7. 10. 3), we rewrite (3) in the form

$$\begin{aligned}
\ln (K/\text{atm}) = & - (H^0_{CO_2}/RT - \ln \lambda^{\dagger}_{CO_2}) \\
& - (H^0_C/RT - \ln \lambda_C) \\
& + 2 (H^0_{CO}/RT - \ln \lambda^{\dagger}_{CO}) \\
& - \frac{\Delta H^0}{RT} \qquad\qquad 7.\ 13.\ 4
\end{aligned}$$

where ΔH^0 is defined by

$$\Delta H^0 = 2H^0_{CO} - H^0_{CO_2} - H^0_C \qquad 7.\ 13.\ 5$$

In these formulae H^0_C denotes the value of the molar heat function of graphite at $T = 0$.

We now evaluate the several terms of (4), beginning with the last. The heat of reaction at 25 °C is given experimentally by

$$\Delta H = 172.47\ \text{kJ} \qquad (T = 298.15\ °K) \qquad 7.\ 13.\ 6$$

For the sake of brevity we denote this temperature by T'. We have then

$$\frac{\Delta H(T')}{R} = \frac{172470}{8.3147} \text{ deg} = 20743 \text{ deg} \qquad 7.\,13.\,7$$

We now write down the identity

$$\begin{aligned}
\Delta H(T') &= 2H_{\text{CO}}\,(T') - H_{\text{CO}_2}\,(T') - H_{\text{C}}\,(T') \\
&= 2\,\{H_{\text{CO}}\,(T') - H^0_{\text{CO}}\} - \{H_{\text{CO}_2}\,(T') - H^0_{\text{CO}_2}\} \\
&\quad - \{H_{\text{C}}\,(T') - H^0_{\text{C}}\} + \Delta H^0 \qquad 7.\,13.\,8
\end{aligned}$$

We have according to (7. 10. 10)

$$2\,\{H_{\text{CO}}\,(T') - H^0_{\text{CO}}\}/R = 2088 \text{ deg} \qquad 7.\,13.$$

and according to (7. 10. 8)

$$\{H_{\text{CO}_2}\,(T') - H^0_{\text{CO}_2}\}/R = 1126 \text{ deg} \qquad 7.\,13.\,10$$

We also have by direct calorimetry

$$\{H_{\text{C}}\,(T') - H^0_{\text{C}}\}/R = 127 \text{ deg} \qquad 7.\,13.\,11$$

Substituting (7), (9), (10), (11) into (8), we obtain

$$\begin{aligned}
\Delta H^0/R &= \{20743 - 2088 + 1126 + 127\} \text{ deg} \\
&= 19908 \text{ deg} \qquad 7.\,13.\,12
\end{aligned}$$

Consequently at 1000 °K the last term of (4) has the value

$$-\frac{\Delta H^0}{RT} = -19.91 \quad (T = 1000 \text{ °K}) \qquad 7.\,13.\,13$$

We turn now to the other three terms of (4). Of these the first and third can be taken from table 7. 1. There remains the second one relating to graphite. As this relates to a solid phase it cannot be computed from spectroscopic data, but must be evaluated from calorimetric data. To be precise H_m has to be measured for solid graphite as a function of T throughout the whole temperature range from 1000 °K down to a temperature so low that extrapolation to $T = 0$ can be made as described in § 4. 36. Such measurements give directly

$$\{H\,(1000) - H^0\}/R = 1547 \text{ deg} \qquad 7.\,13.\,14$$

and by the use of

$$S = \int \frac{dH}{T} \qquad 7.\,13.\,15$$

they give

$$\{S_m\,(1000) - S_m\,(0)\}/R = 2.942 \qquad 7.\,13.\,16$$

But according to our conventional zero of entropy, the molar entropy of graphite is zero at 0 °K. Hence (16) reduces to

$$S_m(1000)/R = 2.942 \qquad \text{7. 13. 17}$$

We therefore have for graphite at 1000 °K, using (14) and (17),

$$\frac{H^0}{RT} - \ln \lambda = \frac{H^0}{RT} - \frac{\mu}{RT} = \frac{H^0}{RT} - \frac{H_m}{RT} + \frac{S_m}{R}$$

$$= -1.547 + 2.942$$

$$= 1.39_5 \qquad (T = 1000 \text{ °K}) \qquad \text{7. 13. 18}$$

Finally substituting into (4) from (13), (18) and table 7. 1, we obtain

$$\ln(K/\text{atm}) = -27.22 - 1.40 + 24.55 + 24.55 - 19.91$$

$$= 0.57$$

or $\qquad K = 1.8 \text{ atm} \qquad (T = 1000 \text{ °K}) \qquad$ 7. 13. 19

The accuracy of a calculation of this kind is at best about ± 0.05 in each term of $\ln K$. This usually leads to an uncertainty of at least 0.1 in $\ln K$ or 10 % in K. In most cases the experimental uncertainty in a direct measurement of K is greater than this.

Whereas to determine the equilibrium constant of a purely gaseous reaction the only calorimetric result required is a value of ΔH at a single temperature, we see from the above example that in an equilibrium involving solids we require in addition calorimetric measurements on the solid right down to temperatures so low that extrapolation to $T = 0$ can be safely performed.

§ 7. 14 REACTIONS BETWEEN PURE SOLIDS OR LIQUIDS

We must now consider reactions between pure solid phases without any gases. Examples are

$$\text{Pb} + 2\text{I} \rightarrow \text{PbI}_2 \qquad \text{7. 14. 1}$$

$$\text{Cu} + \text{S} \rightarrow \text{CuS} \qquad \text{7. 14. 2}$$
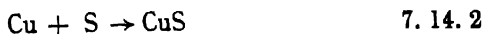
Incidentally, for the following considerations it is immaterial whether any of the phases is a pure liquid instead of a pure solid. As an example we may mention

$$\text{Hg} + \text{AgCl} \rightarrow \text{Ag} + \text{HgCl} \qquad \text{7. 14. 3}$$
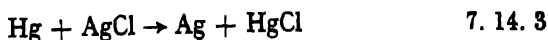
The simplest type of reaction between solid phases is a simple allotropic change, such as

$$\text{rhombic sulphur} \rightarrow \text{monoclinic sulphur} \qquad 7.\,14.\,4$$

$$\text{grey tin} \rightarrow \text{white tin} \qquad 7.\,14.\,5$$

The equilibrium condition for a reaction involving pure solid and liquid phases can still be expressed in the form (7. 01. 9)

$$\Pi\,(\lambda) = 1 \qquad \text{(equilibrium)} \qquad 7.\,14.\,6$$

but each λ is now a function of temperature only, if we disregard the small effect of changes of pressure. Hence the equilibrium condition (6) may be regarded as an equation determining the temperature of reversal of the change considered. This equation may or may not have a solution for T positive. Reactions (1), (2), (3) proceed naturally towards the right at all temperatures and there is no solution of (6). In point of fact very few reactions between pure solids and pure liquids have a reversal temperature. The only important exceptions are allotropic changes such as (4) and (5), among which we may, if we like, include simple fusion.

For reactions such as (1), (2), (3) at all temperatures we have

$$\Pi\,(\lambda) < 1 \qquad 7.\,14.\,7$$

or, taking logarithms and writing in full,

$$\Sigma\,\nu_A \ln \lambda_A > \Sigma\,\nu_B \ln \lambda_B \qquad 7.\,14.\,8$$

or

$$\Sigma\,\nu_A \mu_A > \Sigma\,\nu_B \mu_B \qquad 7.\,14.\,9$$

Another way of expressing the same thing is to state that the affinity A, defined in § 1. 50 is positive at all temperatures. We shall see in chapter 9 how this affinity can often be accurately determined by measurements of electromotive force.

We shall now consider (6) in more detail and for this purpose, we write it in the expanded form

$$\Sigma\,\nu_A \ln \lambda_A = \Sigma\,\nu_B \ln \lambda_B \qquad 7.\,14.\,10$$

But by definition

$$\ln \lambda = \frac{\mu}{RT} = \frac{H_m}{RT} - \frac{S_m}{R} \qquad 7.\,14.\,11$$

Substituting (11) into (10), we obtain

$$T = \frac{\Sigma\,\nu_B H_B - \Sigma\,\nu_A H_A}{\Sigma\,\nu_B S_B - \Sigma\,\nu_A S_A} \qquad 7.\,14.\,12$$

The numerator of (12) is the heat of reaction ΔH and the denominator is the entropy of reaction ΔS. We now consider these separately.

For ΔH we write formally

$$\Delta H(T) = \Delta H(T') + \Sigma \, \nu_B \{H_B(T) - H_B(T')\}$$
$$- \Sigma \, \nu_A \{H_A(T) - H_A(T')\} \qquad 7.\,14.\,13$$

If for each of the substances the dependence of H on temperature has been determined calorimetrically and if in addition ΔH has been measured at any one temperature T', then by means of (13) ΔH can be calculated at any other temperature.

For ΔS we write formally

$$\Delta S(T) = \Delta S^0 + \Sigma \, \nu_B \{S_B(T) - S_B^0\} - \Sigma \, \nu_A \{S_A(T) - S_A^0\} \qquad 7.\,14.\,14$$

where the supercript ^{0} denotes the value obtained by smooth extrapolation to $T = 0$. If now the dependence of H on temperature has been measured throughout the temperature range from T down to a temperature from which one can extrapolate to $T = 0$, then (14) determines ΔS for all temperatures apart from the constant ΔS^0. But S^0 is the quantity discussed in detail in §§ 4. 60—4. 66. It has the value zero except for a few well understood exceptions for which its value is known to be $R \ln o$, with o a small number such as 2 or $\frac{3}{2}$. With this knowledge of ΔS^0, or in the absence of evidence to the contrary assuming $\Delta S^0 = 0$, formula (14) determines ΔS for all temperatures.

Using (13) and (14) together, we can solve (12) for the *transition temperature* T. Alternatively using the experimental value of T, we can use (12), (13), (14) to determine an experimental value for ΔS^0.

§ 7. 15 TRANSITION OF SULPHUR

We shall now illustrate the formulae of the preceding section by a numerical example. As already mentioned it is difficult to find an example of an equilibrium temperature for a reaction between solid phases except in the simplest case of an allotropic change. We accordingly choose as our example

$$\text{rhombic sulphur} \rightarrow \text{monoclinic sulphur} \qquad 7.\,15.\,1$$
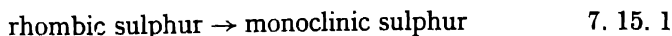
and we shall use the subscripts $_R$ and $_M$ for the rhombic and monoclinic forms respectively. The transition temperature is

$$T = 368.6 \, °K \qquad \text{(transition)} \qquad 7.\,15.\,2$$

The heat of transition at this temperature is

$$\frac{\Delta H}{R} = \frac{H_M - H_R}{R} = 47.5 \pm 5 \text{ deg} \qquad (T = 368.6 \text{ °K}) \qquad 7.15.3$$

Consequently the entropy of transition at this temperature is

$$\frac{\Delta S}{R} = \frac{S_M - S_R}{R} = \frac{47.5}{368.6} = 0.12 \pm 0.01 \qquad (T = 368.6 \text{ °K}) \qquad 7.15.4$$

According to calorimetric measurements * on the two forms from 15 °K to the transition temperature

$$\frac{S_R(368.6°) - S_R(15°)}{R} = 4.38 \pm 0.03 \qquad 7.15.5$$

$$\frac{S_M(368.6°) - S_M(15°)}{R} = 4.49 \pm 0.04 \qquad 7.15.6$$

Combining (4), (5) and (6) we obtain

$$\frac{S_M(15°) - S_R(15°)}{R} = 0.12 - 4.49 + 4.38$$

$$= 0.01 \pm 0.05 \qquad 7.15.7$$

We conclude that well within the experimental accuracy

$$S_M^0 - S_R^0 = 0. \qquad 7.15.8$$

§ 7.16 HOMOGENEOUS EQUILIBRIUM IN SOLUTION

We turn now to homogeneous chemical equilibrium in a liquid solution. We again start from the general equilibrium condition (7.01.9)

$$\Pi(\lambda) = 1 \qquad 7.16.1$$

and use (6.11.4)

$$\lambda = \lambda^\ominus m\gamma \qquad 7.16.2$$

Substituting (2) into (1) we obtain

$$\Pi(m)\,\Pi(\gamma) = K_m \qquad 7.16.3$$

where K_m is defined by

$$K_m^{-1} = \Pi(\lambda^\ominus) \qquad 7.16.4$$

* For details of experimental data, see Eastman and McGavock, *J. Amer. Chem. Soc.* 1937 **59** 145.

and so depends only on the solvent and the temperature. K_m is called the *molality equilibrium constant*. Formula (3) tells us that the equilibrium molality quotient is inversely proportional to the equilibrium activity-coefficient quotient.

In the special case of an ideal dilute solution (3) reduces to

$$\Pi\,(m) = K_m \qquad\qquad 7.\,16.\,5$$

§ 7. 17 TEMPERATURE DEPENDENCE

If we take logarithms of (4) and write them in full we have

$$\ln K_m = \Sigma\,\nu_A \ln \lambda_A^\ominus - \Sigma\,\nu_B \ln \lambda_B^\ominus \qquad\qquad 7.\,17.\,1$$

Differentiating with respect to T and using (6. 14. 2) and (6. 08. 8) we obtain

$$\frac{\partial \ln K_m}{\partial T} = \frac{\Sigma\,\nu_B\,H_B^\infty - \Sigma\,\nu_A\,H_A^\infty}{RT^2} = \frac{\Delta H^\infty}{RT^2} \qquad\qquad 7.\,17.\,2$$

where ΔH^∞ is the *heat of reaction* at infinite dilution in the given solvent.

§ 7. 18 USE OF VOLUME CONCENTRATIONS

As mentioned in § 6. 30 volume concentrations are sometimes used instead of molalities but the practice is not recommended. In place of (7. 16. 3) one then obtains

$$\Pi\,(c)\,\Pi\,(y) = K_c \qquad\qquad 7.\,18.\,1$$

where c denotes concentration and y denotes a different kind of activity coefficient. We shall not go into details, but will only emphasize that the temperature dependence of K_c is given by [*]

$$\frac{\partial \ln K_c}{\partial T} \qquad \frac{\Delta H^\circ}{RT^2} \qquad a\Delta\nu \qquad\qquad 7.\,18.\,2$$

where a denotes the coefficient of thermal (cubical) expansion of the solvent. Spurious formulae for $\partial \ln K_c/\partial T$ have sometimes been quoted and have been obtained by false analogy with gaseous equilibria.

§ 7. 19 HETEROGENEOUS EQUILIBRIA INVOLVING SOLUTIONS

We might also discuss equilibria involving solutions and vapour phases, or solutions and solids or even solutions, solids and vapour

[*] Guggenheim, *Trans. Faraday Soc.* 1937 **33** 607 formula 4. 8.

phases, but this is unnecessary, because any equilibrium however complicated can be regarded as a superposition of a homogeneous equilibrium in a single phase, liquid or gaseous, and distribution equilibria of individual species between pairs of phases. Both these elementary types of equilibrium have been discussed in sufficient detail.

§ 7. 20 TRANSITIONS OF SECOND ORDER

This is perhaps the most convenient place to describe a phenomenon called a *transition of the second order*. It is quite different from anything we have yet met, having some of the characteristics of phase changes and some of the characteristics of critical phenomena. We shall first show by a particular example how a transition of the second order arises from certain assumed properties of the thermodynamic functions. We shall then discuss briefly how and when they occur.

As a preliminary step to our discussion, we shall consider the thermodynamic properties of the equilibrium between two isomers under the simplest conceivable conditions. Thus we consider the isomeric change

$$A \to B \qquad\qquad 7.\,20.\,1$$

occurring in a mixture of A and B in the absence of any other species. We further assume that the mixture is ideal. Finally we assume that the heat of reaction has a value w independent of the temperature; in other words we assume that A and B have equal heat capacities. If then x denotes the mole fraction of B the molar Gibbs function G_m has the form

$$\frac{G_m}{RT} = \frac{G_m^0\,(T)}{RT} + \frac{w}{RT}\,x + (1 - x) \ln\,(1 - x) + x \ln x \qquad 7.\,20.\,2$$

where w is a constant and $G_m^0\,(T)$ depends only on the temperature. From (2) we deduce

$$H_m = G_m^0 - T\,\frac{dG_m^0}{dT} + wx \qquad\qquad 7.\,20.\,3$$

from which we verify that the heat of reaction is w. We also deduce

$$\frac{S_m}{R} = -\frac{1}{R}\,\frac{dG_m^0}{dT} - (1 - x) \ln\,(1 - x) - x \ln x \qquad 7.\,20.\,4$$

showing that the molar entropy of mixing has its ideal value

$$- R\,\{(1 - x) \ln\,(1 - x) + x \ln x\} \qquad\qquad 7.\,20.\,5$$

The equilibrium value of x is obtained by minimizing G_m. We find

$$\frac{1}{RT} \frac{\partial G_m}{\partial x} = \frac{w}{RT} + \ln \frac{x}{1-x} = 0 \qquad 7.\,20.\,6$$

so that

$$\frac{x}{1-x} = \mathrm{e}^{-w/RT} \qquad 7.\,20.\,7$$

Formula (7) is, of course, the simplest possible example of the equilibrium law. Before we dismiss this extremely simple system, there remains one important point to be investigated, namely the verification that (6) and (7) do correspond to a minimum of G_m, not to a maximum. We have

$$\frac{1}{RT} \frac{\partial^2 G_m}{\partial x^2} = \frac{1}{x} + \frac{1}{1-x} > 0 \qquad 7.\,20.\,8$$

thus verifying that we have found a minimum, not a maximum.

Let us now arbitrarily introduce a modification into the form of G_m assumed in (2), without at this stage enquiring into the physical significance of the change. We replace the term wx by $wx(1-x)$. We then have

$$\frac{G_m}{RT} = \frac{G_m^0(T)}{RT} + \frac{wx(1-x)}{RT} + (1-x)\ln(1-x) + x \ln x \qquad 7.\,20.\,9$$

$$H_m = G_m^0 - T \frac{\mathrm{d}G_m^0}{\mathrm{d}T} + wx(1-x) \qquad 7.\,20.\,10$$

$$\frac{S_m}{R} = -\frac{1}{R} \frac{\mathrm{d}G_m^0}{\mathrm{d}T} - (1-x)\ln(1-x) - x \ln x \qquad 7.\,20.\,11$$

from which we observe that the heat function is affected by the modification, but the entropy is not.

We now seek the equilibrium value of x by minimizing G_m. We find

$$\frac{1}{RT} \frac{\partial G_m}{\partial x} = -\frac{w}{RT}(2x-1) + \ln \frac{x}{1-x} = 0 \qquad 7.\,20.\,12$$

so that

$$\frac{x}{1-x} = \exp\{(2x-1)\,w/RT\} \qquad 7.\,20.\,13$$

One solution of (13) is obviously $x = \frac{1}{2}$, but this is not always the

only solution. Nor is this solution necessarily a minimum rather than a maximum of G_m. We must investigate these points and shall do so in the first place graphically. Fig. 7. 1 shows $(G_m - G_m^0)/RT$ plotted against $2(x - \frac{1}{2})$ for various values of $\frac{1}{2}w/RT$. Owing to the complete symmetry between x and $1 - x$, we can without loss of generality assume that $x > 1 - x$.

We see that, when $w > 0$, at high temperatures, that is small values of w/RT, the root $x = \frac{1}{2}$ is the only root and it corresponds to a minimum of G_m. At low enough temperatures, that is large values of w/RT, there is another root $\frac{1}{2} < x < 1$ and this root corresponds to a minimum of G_m while the root $x = \frac{1}{2}$ now corresponds to a maximum. Thus there exists a temperature T_λ such that at temperatures below T_λ the equilibrium value of x is greater than $\frac{1}{2}$ and decreases as the temperature increases; the equilibrium value of x becomes $\frac{1}{2}$ at the temperature T_λ and remains $\frac{1}{2}$ at all higher temperatures. The change occurring at the temperature T_λ is called a *transition of the second order* and the temperature T_λ is called a *lambda point* for a reason which will be explained later.
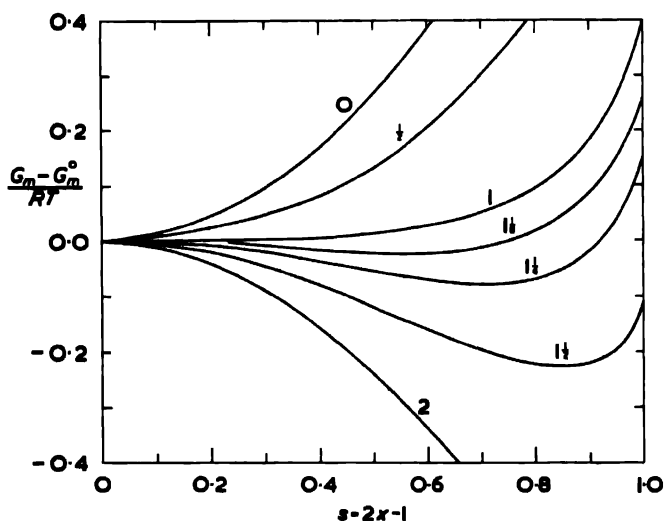
Fig. 7. 1. Dependence of G_m on x for various values of $\frac{1}{2}w/RT$. The numbers attached to the curves are values of $\frac{1}{2}w/RT$ or T_λ/T.

It is clear from fig. 7. 1 that T_λ is the temperature at which the two roots of (13) become equal, the root at $x = \frac{1}{2}$ changing from a minimum

to a maximum. Thus there is a point of horizontal inflexion at $x = \frac{1}{2}$, $T = T_\lambda$. We have then

$$\frac{1}{RT} \frac{\partial^2 G_m}{\partial x^2} = - \frac{2w}{RT_\lambda} + \frac{1}{x} + \frac{1}{1-x} = 0 \qquad (x = \tfrac{1}{2}) \qquad 7.\,20.\,14$$

whence

$$\frac{w}{RT_\lambda} = 2 \qquad\qquad\qquad 7.\,20.\,15$$

It is clear from fig. 7. 1 that for negative values of w the minimum is always at $x = \frac{1}{2}$ and there can be no lambda point.

§ 7. 21 COOPERATIVE SYSTEMS

Before proceeding to a more detailed examination of transitions of the second order, we shall explain in very general terms how they may arise. As a preliminary step, let us determine the *molar heat of change* in the process (7. 20. 1). For the heat function H of the whole system, we have according to (7. 20. 10) changing to the variables n_A, n_B

$$H = (n_A + n_B) H^0 + \frac{n_A\, n_B}{n_A + n_B} w \qquad\qquad 7.\,21.\,1$$

where H^0 is independent of n_A, n_B. Differentiating with respect to n_A, n_B in turn we obtain for the partial molar heat functions

$$H_A = H^0 + \frac{n_B^2}{(n_A + n_B)^2} w = H^0 + x^2 w \qquad\qquad 7.\,21.\,2$$

$$H_B = H^0 + \frac{n_A^2}{(n_A + n_B)^2} w = H^0 + (1 - x)^2 w \qquad\qquad 7.\,21.\,3$$

so that the molar *heat of change* from A to B is

$$H_B - H_A = (1 - 2x)w \qquad\qquad 7.\,21.\,4$$

Since we are considering a condensed phase (4) is essentially equivalent to

$$U_B - U_A = (1 - 2x)w \qquad\qquad 7.\,21.\,5$$

The outstanding characteristic of (5) is that the energy required to convert a molecule A into a molecule B depends in a marked degree on what fraction of all the molecules is present in each form. Such a characteristic would not be expected when the process

$$A \to B \qquad\qquad 7.\,21.\,6$$

represents a chemical change of one isomer to another, nor in such a case do we find a lambda point. It is however not difficult to mention other interpretations of (6) which might reasonably be expected to have the characteristic just mentioned. Suppose for example we consider a regular array of polar molecules or atoms in a lattice. Suppose further that each molecule or atom can point in either of two opposite directions. Suppose finally that we denote the molecules by A or B according to the direction in which they point. Then it is easily understandable that the energy required to turn round a molecule or atom may depend markedly on how many other molecules or atoms are pointing in either direction. This behaviour is typical of systems called *cooperative*. The significance of the name should be clear from this and the following examples.

Another more complicated, but possibly more important, interpretation of (6) is for A to represent a state of molecular libration and B a state of molecular rotation.

Another example occurring in certain alloys is the following. Suppose we have an alloy of the composition ZnCu containing N atoms of Zn and N atoms of Cu arranged on a regular lattice of $2N$ lattice points. We can picture two extreme arrangements of the two kinds of atoms on the lattice, one completely ordered, the other completely random. In the completely ordered arrangement every alternate lattice point A is occupied by a Zn atom and the remaining lattice points B are occupied by Cu atoms. In the opposite extreme arrangement every lattice point A or B is occupied by either Zn or Cu atoms arranged at complete random. We can moreover consider intermediate arrangements such that a fraction x of the Zn atoms occupy A lattice points and the fraction $(1 - x)$ of Zn atoms occupy B lattice points. The remaining lattice points are of course occupied by the Cu atoms. We can then without loss of generality take $x \geqslant \frac{1}{2}$. In such a system the average energy required to move a Zn atom from an A point to a B point will depend markedly on how many A points are already occupied by Zn atoms. It is therefore at least conceivable that such a system might have a lambda point.

As a matter of fact the alloy having the composition ZnCu does have a lambda point and the thermodynamic properties of this system can be at least semi-quantitatively represented by a Gibbs function of the form (7. 20. 9). This form was first suggested by Gorsky * and later independently derived by approximate statistical considerations by

* Gorsky, Z. Phys. 1928 **50** 64.

Bragg and Williams *. It is outside the scope of this book to consider this aspect of the phenomenon and we shall accordingly confine ourselves to a purely phenomenological thermodynamic investigation of some of the general properties of lambda points, among others the property leading to the name.

§ 7. 22 ALTERNATIVE NOTATION

The notation which we have used to introduce the subject of *transitions of the second order* is the one which seems natural. It is not however the notation most used. For the sake of completeness we describe briefly the alternative notation.

A quantity s called the *degree of order* is defined by *

$$s = 2x - 1 \qquad\qquad 7.\,22.\,1$$

or

$$x = \tfrac{1}{2}(1 + s) \qquad\qquad 7.\,22.\,2$$

In this notation formula (7. 20. 9) becomes

$$\frac{G_m}{RT} = \frac{G_m^0}{RT} + \frac{w}{RT}\frac{1 - s^2}{4}$$
$$+ \tfrac{1}{2}(1 + s)\ln(1 + s) + \tfrac{1}{2}(1 - s)\ln(1 - s) - \ln 2 \qquad 7.\,22.\,3$$

The equilibrium value of s is determined according to (7. 20. 12) by

$$\ln\frac{1 + s}{1 - s} = \frac{w}{RT}\,s \qquad\qquad 7.\,22.\,4$$

which is equivalent to

$$\tanh\frac{ws}{2RT} = s \qquad\qquad 7.\,22.\,5$$

Using (7. 20. 15) we can transform (5) to

$$\frac{T_\lambda}{T} = \frac{\tanh^{-1}s}{s} \qquad\qquad 7.\,22.\,6$$

These formulae, of course, contain nothing which is not already contained in the formulae of § 7. 20. It is merely a historical accident that pioneer workers in this field used the variable s instead of x.

Bragg and Williams, *Proc. Roy. Soc.* A 1934 **145** 699.

§ 7. 23 CHARACTERISTICS OF LAMBDA POINT

We have seen how a Gibbs function of the form (7. 20. 9) leads without any further assumption to the occurrence of a *transition of the second order* and we have explained how this type of behaviour can occur in a *cooperative system*. We do not assert that a Gibbs function of approximately this form is the origin of all transitions of the second order. Still less do we assert that a Gibbs function of this form accounts accurately for any transition of the second order. We merely assert that the form (7. 20. 9) of the Gibbs function is one possible form which leads to the occurrence of a lambda point having certain general characteristics which we shall describe. We shall continue to make use of the particular forms of thermodynamic functions described in § 7. 20 for illustrative purposes.

From fig. 7. 1, or more accurately by calculation from (7. 20. 13), we can determine the equilibrium value of x as a function of T. The
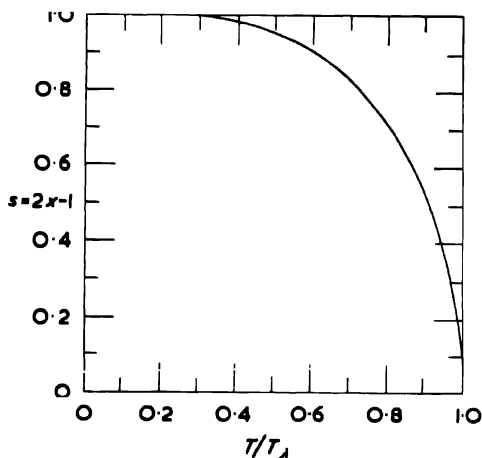
Fig. 7. 2. Dependence of equilibrium value of degree of order on temperature.

result is given in fig. 7. 2, where $s = 2x - 1$ is plotted against T/T_λ. We notice that at temperatures immediately below T_λ the equilibrium value of s changes rapidly with temperature and at temperatures below $\frac{1}{2}T_\lambda$ this equilibrium value hardly differs appreciably from unity. There is then a rapid change of the equilibrium value of s in the temperature range between T_λ and $\frac{1}{2}T_\lambda$. Associated with this change in s there is a rapid change in the part of the molar energy or heat function which depends on s, namely the term

$$wx(1 - x) = \tfrac{1}{4}w(1 - s^2) \qquad\qquad 7. 23. 1$$

This is shown in fig. 7. 3. The term (1) occurs in the energy additional to other terms due to the translational and internal degrees of freedom of
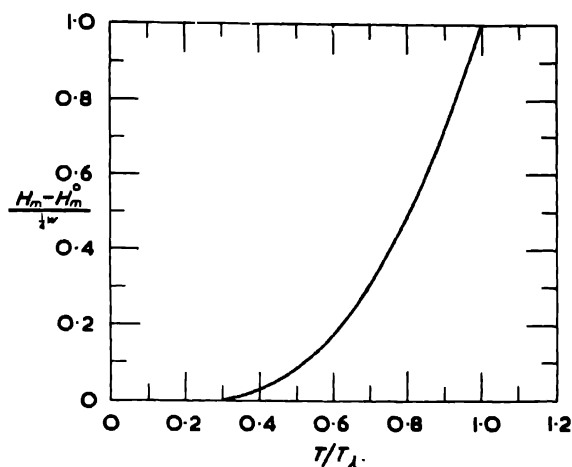
Fig. 7. 3. Temperature dependence of heat function due to variation in degree of order.

the molecules. Thus as the temperature is decreased through the lambda point there is a sudden change in the temperature coefficient of the heat function, or in other words a discontinuity in the heat capacity C. This is shown in fig. 7. 4. The shape of the curve recalls a Greek capital Λ whence the name *lambda point* suggested by Ehrenfest [*].
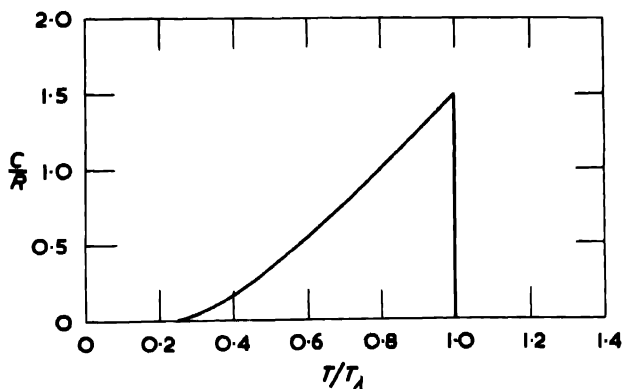
Fig. 7. 4. Contribution to heat capacity of variation in degree of order.

[*] See Keesom, *Helium* 1942 p. 216.

For the particular model considered in detail, we observe that in the immediate neighbourhood below the lambda temperature

$$\frac{\partial H}{\partial s} = 0 \qquad\qquad 7.\,23.\,2$$

$$\frac{\partial S}{\partial s} = 0 \qquad\qquad 7.\,23.\,3$$

$$\frac{ds}{dT} = \infty \qquad\qquad 7.\,23.\,4$$

in such a manner that

$$\frac{\partial H}{\partial s}\,\frac{ds}{dT} \text{ is finite} \qquad\qquad 7.\,23.\,5$$

$$\frac{\partial S}{\partial s}\,\frac{ds}{dT} \text{ is finite} \qquad\qquad 7.\,23.\,6$$

The properties (5) and (6) are characteristic of all lambda points and are independent of the choice of s. On the other hand the relations (2), (3), (4) depend on the definition of s. For example if we replace s by $\sigma = s^2$, then

$$\frac{\partial H}{\partial \sigma} \text{ is finite} \qquad\qquad 7.\,23.\,7$$

$$\frac{\partial S}{\partial \sigma} \text{ is finite} \qquad\qquad 7.\,23.\,8$$

We may then describe a transition of the second order as a discontinuity in C, with continuity of H, S, G, at a certain temperature T_λ called the *lambda point*.

The lambda point known longest is the one discovered by Curie and therefore called the *Curie point*, below which a substance such as iron has permanent magnetization and above which it has not. The Curie point will be referred to again in chapter 12.

Probably the most interesting, most studied but least understood lambda point is that of helium at 2.2 °K. The experimental data * for C plotted against T are shown in fig. 7. 5.

Many other lambda points are known to occur in crystals and are usually associated with a sudden change in the extent to which the

* Keesom, *Helium* 1942 p. 215.

molecules in the crystal can rotate freely. Few however, if any, have been studied in such detail as to be completely understood.

§ 7. 24 COMPARISON WITH PHASE CHANGE AND CRITICAL POINT

Since a substance has measurably different properties above and below the lambda point, there is a temptation to regard a *transition of the second order* as a kind of *phase change*. The expression *phase change of the second order* has been used, but as it has in the past led to considerable confusion it is better avoided *
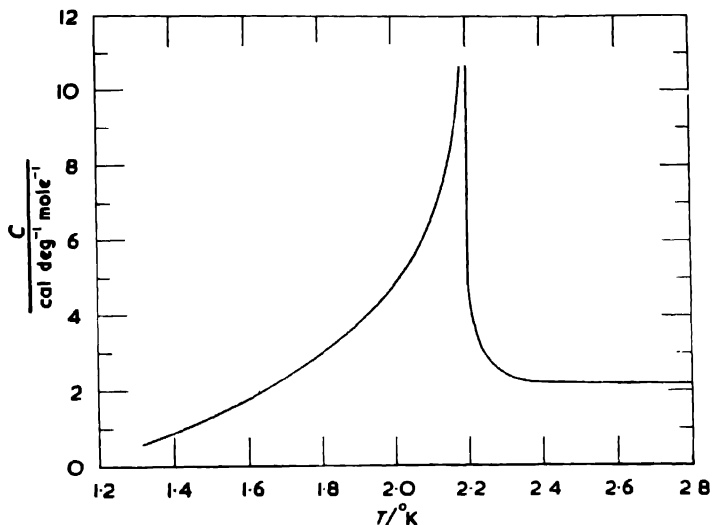
Fig. 7. 5   Heat capacity of liquid helium near lambda point.

The contrast between a lambda point and a phase change may be made clear by a plot of the molar Gibbs function against the temperature. This is shown in fig. 7. 6. Diagram A depicts a phase change. The
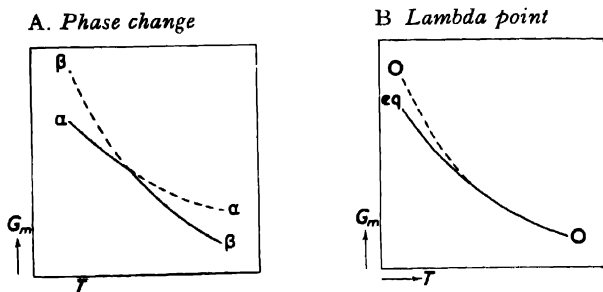
Fig. 7. 6. Contrast between phase change and lambda point.

* Guggenheim, *Proc. Acad. Sci. Amst.* 1934 **37** 3.

curves of the two distinct α and β cut at the transition point, the dotted portions of the curves representing metastable states. Diagram B depicts a transition of the second order. The curve marked O represents the Gibbs function of a hypothetical phase with $s = 0$, which is usually associated with complete randomness. The curve marked eq represents the Gibbs function of a phase in which at each temperature s has its equilibrium value. Below the lambda point the dotted curve marked O lies above the curve marked eq and consequently the former represents metastable states.

At the lambda point the two curves touch. We might ask what happens to the eq curve above the lambda point. If we extend the eq curve by the simplest analytical formula, ignoring physics, the curve would continue below the O curve, thus suggesting that it represents states more stable than the O curve. On further study we should however find that this hypothetical curve corresponds to negative values of s^2 and has therefore no physical meaning. It is therefore safer and more profitable to forget about such a curve.

On the other hand a comparison between a lambda point and a critical point, if not carried too far, is less dangerous. At temperatures below the lambda point there is a stable phase with a value of s determined by the temperature and there can also be a metastable phase with $s = 0$; the latter can in fact sometimes be realized in practice by sudden chilling from a temperature above the lambda point. The difference between these two phases, measured by the values of s, gradually decreases as the temperature is raised and vanishes at the lambda point when the two phases become identical. This recalls the behaviour of liquid and vapour phases at the critical point, but here the resemblance ends.

§ 7. 25 DEPENDENCE OF LAMBDA POINT ON PRESSURE

Up to this point we have considered how a transition of the second order occurs at a certain temperature, completely disregarding the pressure. This is in practice justifiable for most such transitions, but in principle there can be a dependence on the pressure. In practice the only known example where pressure changes are likely to be important is that of liquid helium. Let us then consider how the lambda point is affected when the pressure is changed.

In the particular model represented by (7. 20. 9) the dependence on pressure would result from the energy parameter w being a function of

the pressure. We shall however not assume this model nor any other detailed model, but shall rather derive formulae of great generality.

Regarding G as a function of s, as well as of T, P we have

$$dG = -SdT + VdP + \frac{\partial G}{\partial s}\, ds \qquad\qquad 7.\,25.\,1$$

and differentiating throughout with respect to s

$$d\frac{\partial G}{\partial s} = -\frac{\partial S}{\partial s}\, dT + \frac{\partial V}{\partial s}\, dP + \frac{\partial^2 G}{\partial s^2}\, ds \qquad 7.\,25.\,2$$

Now the equilibrium value of s at each temperature is determined by

$$\frac{\partial G}{\partial s} = 0 \qquad \text{(equilibrium)} \qquad 7.\,25.\,3$$

and in particular at the lambda point

$$s = 0 \qquad \text{(lambda point)} \qquad 7.\,25.\,4$$

If then we follow the lambda point at varying pressure we have (3) and owing to (4) we have

$$ds = 0 \qquad \text{(lambda point)} \qquad 7.\,25.\,5$$

Substituting (3) and (5) into (2) we obtain

$$-\frac{\partial S}{\partial s}\, dT + \frac{\partial V}{\partial s}\, dP = 0 \qquad \text{(lambda point)} \qquad 7.\,25.\,6$$

or

$$\frac{dT_\lambda}{dP} = \frac{\left(\dfrac{\partial V}{\partial s}\right)_{s=0}}{\left(\dfrac{\partial S}{\partial s}\right)_{s=0}} \qquad\qquad 7.\,25.\,7$$

Formula (7) describes in the most general way how the temperature of the lambda point depends on the pressure. The right side of (7) can however usefully be transformed into alternative forms more directly related to experimental data.

We accordingly multiply numerator and denominator of (7) by ds/dT, where s here denotes the equilibrium value. We obtain

$$\frac{dT_\lambda}{dP} = \frac{\dfrac{\partial V}{\partial s}\dfrac{ds}{dT}}{\dfrac{\partial S}{\partial s}\dfrac{ds}{dT}} \qquad\qquad 7.\,25.\,8$$

where every quantity on the right side is given its equilibrium value at or immediately below T_λ. We shall now examine the physical significance of the numerator and denominator on the right of (8).

Let us use the superscripts $^-$ and $^+$ to denote the value of quantities immediately below and immediately above the temperature Then we have

$$G^- = G^+ \qquad\qquad 7.\,25.\,9$$

$$H^- = H^+ \qquad\qquad 7.\,25.\,10$$

$$S^- = S^+ \qquad\qquad 7.\,25.\,11$$

$$C^- = C^+ + T_\lambda \frac{\partial S}{\partial s}\frac{ds}{dT} \qquad\qquad 7.\,25.\,12$$

so that the denominator of the right of (8) is $(C^- - C^+)/T_\lambda$.

Similarly if a denotes coefficient of thermal expansion

$$V^- = V^+ = V_\lambda \qquad\qquad 7.\,25.\,13$$

$$a^-V_\lambda = a^+V_\lambda + \frac{\partial V}{\partial s}\frac{ds}{dT} \qquad\qquad 7.\,25.\,14$$

so that the numerator in (8) is $(a^- - a^+)\,V_\lambda$.

Hence substituting (12) and (14) into (8) we obtain

$$\frac{dT_\lambda}{dP} = \frac{(a^- - a^+)\,V_\lambda\,T_\lambda}{C^- - C^+} \qquad\qquad 7.\,25.\,15$$

This formula shows how the effect of pressure on the lambda point is related to the discontinuities in C and in a.

Returning to (7), instead of multiplying numerator and denominator by ds/dT, we could multiply by ds/dP, obtaining

$$\frac{dT_\lambda}{dP} = \frac{\dfrac{\partial V}{\partial s}\dfrac{ds}{dP}}{\dfrac{\partial S}{\partial s}\dfrac{ds}{dP}} \qquad\qquad 7.\,25.\,16$$

But if $\varkappa$ denotes isothermal compressibility, we have

$$\varkappa^- V_\lambda = \varkappa^+ V_\lambda - \frac{\partial V}{\partial s}\frac{ds}{dP} \qquad \text{7. 25. 17}$$

Similarly

$$\left(\frac{\partial S}{\partial P}\right)^- = \left(\frac{\partial S}{\partial P}\right)^+ + \frac{\partial S}{\partial s}\frac{ds}{dP} \qquad \text{7. 25. 18}$$

and so using Maxwell's relation (3. 04. 4) we have

$$a^- V_\lambda = a^+ V_\lambda - \frac{\partial S}{\partial s}\frac{ds}{dP} \qquad \text{7. 25. 19}$$

Substituting (17) and (19) into (16) we obtain

$$\frac{dT_\lambda}{dP} = \frac{\varkappa^- - \varkappa^+}{a^- - a^+} \qquad \text{7. 25. 20}$$

This formula relates the dependence of the lambda point on the pressure to the discontinuities in a and $\varkappa$.

Formulae (15) and (20) are due to Ehrenfest [*].

§ 7. 26 TRANSITIONS OF HIGHER ORDER

In an ordinary *phase change*, which we may call a *transition of the first order*, we have

$$\left.\begin{array}{l} G \qquad\qquad \text{continuous} \\ S = -\dfrac{\partial G}{\partial T} \quad \text{discontinuous} \end{array}\right\} \begin{array}{l} \text{1st order} \\ \text{transitions} \end{array}$$

In the *transitions of the second order*, which we have been discussing, we have

$$\left.\begin{array}{l} G, \dfrac{\partial G}{\partial T} \qquad\qquad \text{continuous} \\ C = -T\dfrac{\partial^2 G}{\partial T^2} \quad \text{discontinuous} \end{array}\right\} \begin{array}{l} \text{2nd order} \\ \text{transitions} \end{array}$$

In a like manner we can define a *transition of the third order* by

$$\left.\begin{array}{l} G, \dfrac{\partial G}{\partial T}, \dfrac{\partial^2 G}{\partial T^2} \text{ continuous} \\ \dfrac{\partial^3 G}{\partial T^3} \qquad\qquad \text{discontinuous} \end{array}\right\} \begin{array}{l} \text{3rd order} \\ \text{transitions} \end{array}$$

[*] Ehrenfest, *Proc. Acad. Sci. Amst.* 1933 **36** 153.

It is possible that transitions of the third order exist. It is further possible to extend the above definitions to transitions of still higher order. We shall however not pursue this matter any further.

§ 7. 27 COMPONENTS AND DEGREES OF FREEDOM

Since the equilibrium condition for the chemical change

$$\Sigma \nu_A A \rightarrow \Sigma \nu_B B \qquad 7.27.1$$

is given by (7. 01. 5)

$$\Sigma \nu_A \mu_A = \Sigma \nu_B \mu_B \qquad 7.27.2$$

all variations of temperature, pressure and composition consistent with chemical equilibrium must satisfy

$$\Sigma \nu_A \, d\mu_A = \Sigma \nu_B \, d\mu_B \qquad 7.27.3$$

This is a relation between the chemical potentials additional to and independent of the Gibbs-Duhem relations. The existence of this relation reduces by one the number of degrees of freedom of the system.

Let us consider a particular example, namely a gaseous mixture of N_2, H_2 and NH_3. This single phase system can be described by T, P, x_{N_2}, x_{H_2}, x_{NH_3} subject to the identity

$$x_{N_2} + x_{H_2} + x_{NH_3} = 1 \qquad 7.27.4$$

or alternatively by T, P, μ_{N_2}, μ_{H_2}, μ_{NH_3} subject to the Gibbs-Duhem relation

$$x_{N_2} \, d\mu_{N_2} + x_{H_2} \, d\mu_{H_2} + x_{NH_3} \, d\mu_{NH_3} = 0 \qquad 7.27.5$$

Hence in the absence of chemical reaction between the three components the system has four degrees of freedom. If however, for example by introducing a catalyst, we enable the process

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad 7.27.6$$

to attain equilibrium, then there is the further restriction

$$\mu_{N_2} + 3\mu_{H_2} = 2\mu_{NH_3} \qquad 7.27.7$$

which reduces the number of degrees of freedom from four to three. This situation is sometimes described by saying that of the three species N_2, H_2 and NH_3 there are only two *independent components*. Whether or not this terminology is adopted the number of degrees of freedom is certainly three.

As a second example consider the system consisting of PCl_3, Cl_2 and PCl_5. There are three chemical species but owing to the equilibrium condition for the reaction

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2 \qquad\qquad 7.\,27.\,8$$

there are only two independent components. For the gaseous phase alone the situation is similar to that in the system N_2, H_2 and NH_3. There are two independent components in one phase and so three degrees of freedom. If we consider the system consisting of the solid phase PCl_5 together with the gaseous phase we have two independent components in two phases and so two degrees of freedom. This means that there are two independent variables which we shall take to be the temperature T and the stoichiometric ratio r of Cl to P in the gas phase. The temperature determines the equilibrium constant K for the process

$$PCl_5\,(s) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g) \qquad\qquad 7.\,27.\,9$$
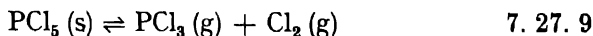
and the partial vapour pressures are then determined by the simultaneous equations

$$p_{PCl_3}\,p_{Cl_2} = K \qquad\qquad 7.\,27.\,10$$

$$\frac{3p_{PCl_3} + 2p_{Cl_2}}{p_{PCl_3}} = r \qquad\qquad 7.\,27.\,11$$

In the particular case $r = 5$ the stoichiometric composition of the gas phase is the same as that of the solid phase PCl_5. In this case some authors go so far as to describe the system as of one component PCl_5. This attitude has nothing to recommend it. We have seen that the system as initially described has two degrees of freedom. These two degrees of freedom are of course reduced to one by specifying the value of r, but the value $r = 5$ has no unique thermodynamic feature. The statement that the ratio of Cl to P in the gas phase is equal to its ratio in the solid phase is no different in kind from the statement that the ratio in the gas phase is one half, or double, the ratio in the solid phase. The distinction between $r = 5$ and other values of r is artificial and pointless. Furthermore it can lead to confusion. Suppose we are interested in the surface phase between solid and gas. Then although the ratio of Cl to P may be 5 in both gas phase and solid there is no reason to expect the ratio to be 5 in the surface phase. In other words there may well be preferential adsorption of either PCl_3 or Cl_2 and this can not be described in terms of the single component PCl_5. Again suppose there is a gravitational field. Then, as we shall see in chapter 10, the proportion of PCl_3 to Cl_2 will vary

from layer to layer and can have the value unity at one height only. It is then essential to treat the system as of two components even though the overall stoichiometric composition may be that of PCl_5.

Now consider a system in which several chemical changes can take place. Some such changes may be expressible as linear combinations of others, but there will always be a definite number of chemical changes which are linearly independent. Consider for example a system consisting of solid graphite and a gaseous mixture O_2, CO, CO_2. Then of the chemical changes

$$C + \tfrac{1}{2}O_2 \rightarrow CO \qquad\qquad 7.\,27.\,12$$
$$C + O_2 \rightarrow CO_2 \qquad\qquad 7.\,27.\,13$$
$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2 \qquad\qquad 7.\,27.\,14$$
$$C + CO_2 \rightarrow 2CO \qquad\qquad 7.\,27.\,15$$

the third is obtained by subtracting the first from the second, while the fourth is obtained by subtracting the third from the first. Thus only two of these changes are independent. By a comparison of (1) and (2) it is clear that independent chemical processes have independent equilibrium conditions, whereas linearly related chemical processes have linearly related equilibrium conditions. Hence each linearly independent chemical equilibrium corresponds to a restrictive relation between the chemical potentials leading to a decrease by unity in the number of degrees of freedom. For example in the two phase system consisting of solid graphite and a gaseous mixture of O_2, CO, CO_2 the effect of the two independent chemical equilibria is to reduce the number of degrees of freedom from four to two; thus the state of the system is completely determined by the temperature and the pressure. Incidentally in this particular system at equilibrium the amount of free O_2 is so small as to be undetectable. The system may therefore be more simply described as a two phase system containing the three species C, CO and CO_2, between which there is a single chemical reaction

$$C + CO_2 \rightarrow 2CO \qquad\qquad 7.\,27.\,16$$

The equilibrium condition for this process reduces the number of degrees of freedom from three to two. Whichever way we consider the system we find that the number of degrees of freedom is two. Whether we regard the system as consisting of four components with two independent chemical processes, of of three components with one independent chemical process or of two independent components is a mere difference of terminology without practical importance.

SOLUTIONS OF ELECTROLYTES

§ 8. 01 CHARACTERISTICS OF STRONG ELECTROLYTES

When certain substances such as common salt are dissolved in water, the solution has a comparatively high conductivity showing that charged ions must be present. We owe to Arrhenius the suggestion that for these substances, called *strong electrolytes*, the solute is composed largely of the free ions, such as Na^+ and Cl^- in the case of common salt. Study of the optical properties by Bjerrum * led him in 1909 to the conclusion that at least in dilute solutions there are at most very few undissociated molecules and in many such cases the properties of the solution can be accurately accounted for on the assumption that no undissociated molecules are present.

It would be outside the province of this book to discuss whether a dilute solution of a strong electrolyte contains a small fraction of undissociated molecules or none at all. All that matters is that the description of a salt solution as completely dissociated into independent ions, though admittedly an oversimplification, is at least an incomparably better model than one which ignores dissociation into ions. It is in fact a better model than any other of equal simplicity. We shall therefore compare the properties of every real solution of strong electrolytes with an idealized solution containing independent ions.

§ 8. 02 IONIC MOLALITIES

In accordance with the programme outlined in the previous section, we describe the composition of solutions of electrolytes in terms of the ions, not in terms of the undissociated molecules. We accordingly describe the composition of a solution containing one or more electrolytes by the *mole ratio* r_i of each ionic species i defined by

$$r_i = \frac{n_i}{n_1} \qquad 8.\ 02.\ 1$$

* Bjerrum, *Proc. 7th Int. Cong. Pure and Applied Chem.* London 1909 Sect. 10 p. 58; *Z. Elektrochem.* 1918 **24** 321.

In practice it is customary instead of *mole ratios* to use *molalities* m_i defined by

$$m_i = \frac{r_i}{M_1} = \frac{n_i}{M_1 n_1} \qquad\qquad 8.02.2$$

where M_1 denotes the molar mass of the solvent, usually expressed in kilograms per mole.

§ 8.03 ELECTRICAL NEUTRALITY

When we carry out our intention of describing the properties of electrolyte solutions in terms of the ionic species, we shall find that most of the formulae have a close resemblance to those for non-electrolytes. There is however one important difference, namely that the molalities m_i of all the ionic species are not independent because the solution as a whole is electrically neutral. We now proceed to express this condition mathematically.

We use the symbol z to denote the charge on an ion measured in units of the charge of a proton, so that for example

For		
	Na^+	$z = 1$
	Ba^{2+}	$z = 2$
	La^{3+}	$z = 3$
	Cl^-	$z = -1$
	SO_4^{2-}	$z = -2$
	PO_4^{3-}	$z = -3$
	$FeC_6N_6^{4-}$	$z = -4$

We call z the *charge number* of the ion.

If then m_i denotes the molality of the ionic species i having a charge number z_i, the condition of *electrical neutrality* of the solution may be written

$$\Sigma_i\, z_i m_i = 0 \qquad\qquad 8.03.1$$

Alternatively if we use the subscript $_+$ to denote positively charged ions or *cations* and $_-$ to denote negatively charged ions or *anions*, then we may write (1) in the alternative form

$$\Sigma_+\, z_+ m_+ = \Sigma_-\, |z_-| m_- \qquad\qquad 8.03.2$$

wherein $|z_-| = -z_-$ is a positive integer.

Owing to the condition of *electrical neutrality* (1) or (2), a solution

containing ionic species, as well as the solvent, has c not $c + 1$ independent components.

§ 8. 04 IONIC ABSOLUTE ACTIVITIES

Since most equilibrium conditions are expressible in a general, yet convenient, form in terms of absolute activities we shall make continual use of the absolute activity λ_i of each ionic species i. By following this procedure we shall in fact obtain formulae closely resembling those already obtained for non-electrolytes. There is however one important difference. We saw in the previous section that if there are c ionic species i and so c ionic molalities m_i, then only $c - 1$ are independent. There must clearly be some analogous or related property of the set of c quantities λ_i. We shall now discover this property by considering the physical significance of the λ_i's first in particular cases and then in general.

Let us consider the distribution of NaCl between two phases, of which at least one a is a solution: the other β may be a solution in a different solvent or the solid phase. We shall now determine the equilibrium condition for NaCl ab initio on the same lines as in § 1. 45 but in terms of Na^+ and Cl^-. We assume the temperature, but not necessarily the pressure, to be the same in the two phases. Suppose now a small quantity dn_{Na^+} of Na^+ and a small quantity dn_{Cl^-} of Cl^- to pass from the phase a to the phase β, the temperature of the whole system being kept constant. Then the increase in the free energy F is given by

$$dF = -P^a \, dV^a - \mu_{Na^+}^a \, dn_{Na^+} - \mu_{Cl^-}^a \, dn_{Cl^-}$$
$$-P^\beta \, dV^\beta + \mu_{Na^+}^\beta \, dn_{Na^+} + \mu_{Cl^-}^\beta \, dn_{Cl^-} \qquad 8. 04. 1$$

By an argument analogous to that of § 1.45, if the two phases are in mutual equilibrium with respect to the NaCl, the process being considered must be reversible and so dF must be equal to the work done on the system. Thus

$$dF = -P^a \, dV^a - P^\beta \, dV^\beta \qquad 8. 04. 2$$

Subtracting (2) from (1) we obtain

$$(\mu_{Na^+}^\beta - \mu_{Na^+}^a) \, dn_{Na^+} + (\mu_{Cl^-}^\beta - \mu_{Cl^-}^a) \, dn_{Cl^-} = 0 \qquad 8. 04. 3$$

The condition for electrical neutrality (8. 03. 2) in this case takes the simple form

$$dn_{Na^+} = dn_{Cl^-} = dn \qquad \text{8. 04. 4}$$

Substituting (4) into (3) we have

$$(\mu_{Na^+}^\beta - \mu_{Na^+}^\alpha + \mu_{Cl^-}^\beta - \mu_{Cl^-}^\alpha)\, dn = 0 \qquad \text{8. 04. 5}$$

or dividing by dn

$$\mu_{Na^+}^\alpha + \mu_{Cl^-}^\alpha = \mu_{Na^+}^\beta + \mu_{Cl^-}^\beta \qquad \text{8. 04. 6}$$

Since according to the definition of λ_i

$$\mu_i = RT \ln \lambda_i \qquad \text{8. 04. 7}$$

we may rewrite (6) as

$$\ln \lambda_{Na^+}^\alpha + \ln \lambda_{Cl^-}^\alpha = \ln \lambda_{Na^+}^\beta + \ln \lambda_{Cl^-}^\beta \qquad \text{8. 04. 8}$$

or

$$\lambda_{Na^+}^\alpha \lambda_{Cl^-}^\alpha = \lambda_{Na^+}^\beta \lambda_{Cl^-}^\beta \qquad \text{8. 04. 9}$$

We thus see that any phase equilibrium relating to NaCl involves only the sum

$$\mu_{Na^+} + \mu_{Cl^-} \qquad \text{8. 04. 10}$$

or the product

$$\lambda_{Na^+} \lambda_{Cl^-} \qquad \text{8. 04. 11}$$

In the same way an equilibrium relating to $BaCl_2$ would involve only the sum

$$\mu_{Ba^{2+}} + 2\mu_{Cl^-} \qquad \text{8. 04. 12}$$

or the product

$$\lambda_{Ba^{2+}} \lambda_{Cl^-}^2 \qquad \text{8. 04. 13}$$

and an equilibrium relating to $LaCl_3$, only the sum

$$\mu_{La^{3+}} + 3\mu_{Cl^-} \qquad \text{8. 04. 14}$$

or the product

$$\lambda_{La^{3+}} \lambda_{Cl^-}^3 \qquad \text{8. 04. 15}$$

and so on.

But it might be asked what about an equilibrium relating to the chloride ion by itself? The answer is that the transfer of a chloride ion, or any other ion alone, from one phase to another involves a transfer of electrical charge, that is to say a flow of current. We shall consider such processes in detail in the following chapter on *electrochemical systems*. Meanwhile as long as we exclude processes involving a flow of current, and in this chapter we do so, we shall meet the μ_i's and λ_i's only in combinations corresponding to zero net electric charge. We can

express this mathematically by stating that the only linear combinations

$$\Sigma_i \, \nu_i\mu_i \qquad\qquad 8.\,04.\,16$$

and the only products

$$\Pi_i \, (\lambda_i)^{\nu_i} \qquad\qquad 8.\,04.\,17$$

which will occur will be those in which the ν_i's satisfy the relation

$$\Sigma_i \, \nu_i z_i = 0 \qquad\qquad 8.\,04.\,18$$

This means that, apart from electrochemical flow of current, with which we are not concerned in this chapter, we could in each phase assign an arbitrary value to the absolute activity λ_i of one ionic species, for instance the chloride ion. The λ_i's of the remaining ions would then be unambiguously determined. Nothing is however gained by thus arbitrarily fixing the values of the λ_i's. We can just as well leave the arbitrary factor in the λ_i's undetermined, knowing that only those combinations (17) of the λ_i's satisfying (18) will ever occur and that in these combinations the arbitrary factors cancel.

§ 8. 05 IDEAL DILUTE AND REAL SOLUTIONS

It would be logical, as in the case of non-electrolytes, first to define an ideal dilute solution of electrolytes and thereafter to compare the properties of real solutions with ideal dilute solutions. Since however no solution of a strong electrolyte is even approximately ideal dilute even at the highest dilution at which accurate measurements can be made, there seems no point in devoting space to such solutions. We therefore pass straight to real solutions, of which ideal dilute solutions are an idealized limiting case.

§ 8. 06 OSMOTIC COEFFICIENT OF THE SOLVENT

We can define the *osmotic coefficient* φ of the solvent in complete analogy with the case where the solute species are non-electrolytes by formula (6. 12. 1) merely replacing r_s by r_i the mole ratio of an ionic species, or m_s by m_i the molality of an ionic species. For electrolyte solutions (6. 12. 1) becomes

$$\ln \frac{\lambda_1}{\lambda_1^0} = \ln \frac{p_1}{p_1^0} = - \varphi \, \Sigma_i \, r_i \qquad\qquad 8.\,06.\,1$$

We shall use (1) to describe the several equilibrium properties of the

solvent. Before doing so we however point out that if the solution contains non-electrolytes as well as electrolytes, the former may be included formally inside the summation Σ_i. We merely treat an electrically uncharged species as if it were an ion with $z = 0$.

§ 8. 07 FREEZING POINT AND BOILING POINT

Formulae (6. 19. 11) and (6. 19. 12) relating the freezing point T of a solution to the freezing point T^0 of the pure solvent, becomes

$$\varphi \, \Sigma_i \, r_i = M_1 \varphi \, \Sigma_i \, m_i = \frac{[\Delta_f H_1^0]}{R} \left(\frac{1}{T} - \frac{1}{T^0} \right) \qquad 8. \, 07. \, 1$$

where $[\Delta_f H_1^0]$ denotes the value of the molar heat of fusion $\Delta_f H_1^0$ of the pure solvent averaged over the reciprocal temperature range $1/T^0$ to $1/T$. In (1) the value of φ is that at the freezing point of the solution.

The relations (6. 20. 1) and (6. 20. 2) between the boiling point T of a solution of involatile solutes and the boiling point T^0 of the pure solvent becomes

$$\varphi \, \Sigma_i \, r_i = M_1 \varphi \, \Sigma_i \, m_i = \frac{[\Delta_e H_1^0]}{R} \left(\frac{1}{T^0} - \frac{1}{T} \right) \qquad 8. \, 07. \, 2$$

where $[\Delta_e H_1^0]$ denotes the value of the molar heat of evaporation $\Delta_e H_1^0$ of the pure solvent averaged over the reciprocal temperature range $1/T$ to $1/T^0$. In (2) the value of φ is that at the boiling point of the solution.

We recall that usually M_1 is expressed in kg mole^{-1} so that m_i is measured in mole kg^{-1}.

§ 8. 08 OSMOTIC PRESSURE

Formula (6. 18. 2) for the osmotic pressure Π becomes for a solution of electrolytes

$$\frac{\Pi[V_1]}{RT} = \varphi \, \Sigma_i \, r_i \qquad 8. \, 08. \, 1$$

§ 8. 09 IONIC ACTIVITY COEFFICIENTS

In analogy with (6. 11. 1) the activity coefficient γ_i of the ionic species i is related to the absolute activity λ_i by

$$\lambda_i = \lambda_i^{\ominus} \, m_i \gamma_i \qquad 8. \, 09. \, 1$$

$$\gamma_i \to 1 \quad \text{as} \quad \Sigma_i \, m_i \to 0 \qquad 8. \, 09. \, 2$$

The proportionality constant $\lambda_i^{\ominus}$ depends on the solvent and the temperature. Furthermore, as explained in § 8. 04 *in each solution* an arbitrary value may be assigned to λ_i for any one ionic species; the values for the remaining ionic species are then determined in that solution.

§ 8. 10 MEAN ACTIVITY COEFFICIENT OF ELECTROLYTE

Let us consider an electrolyte which consists of ν_+ cations R of charge number z_+ and ν_- anions X of charge number z_- so that according to the condition of *electrical neutrality* $\nu_+ z_+ + \nu_- z_- = 0$. The absolute activity $\lambda_{R,X}$ of the electrolyte $R_{\nu_+} X_{\nu_-}$ is then related to the absolute activities of the two ions by

$$\lambda_{R,X} = \lambda_R^{\nu_+} \lambda_X^{\nu_-} \qquad 8.\,10.\,1$$

Substituting (8. 09. 1) into (1) we have

$$\lambda_{R,X} = (\lambda_R^{\ominus} m_R \gamma_R)^{\nu_+} (\lambda_X^{\ominus} m_X \gamma_X)^{\nu_-} \qquad 8.\,10.\,2$$

and in the limit of infinite dilution

$$\lambda_{R,X} \to (\lambda_R^{\ominus} m_R)^{\nu_+} (\lambda_X^{\ominus} m_X)^{\nu_-} \quad \text{as} \quad \Sigma_i\, m_i \to 0 \qquad 8.\,10.\,3$$

Since $\lambda_{R,X}$ and m_R and m_X are all well defined quantities it is clear from (3) that in spite of the indefiniteness in $\lambda_R^{\ominus}$ and $\lambda_X^{\ominus}$ separately, the product $(\lambda_R^{\ominus})^{\nu_+} (\lambda_X^{\ominus})^{\nu_-}$ is completely defined. Returning now to (2) since $\lambda_{R,X}$ and m_R and m_X and, as we have just seen, the product $(\lambda_R^{\ominus})^{\nu_+} (\lambda_X^{\ominus})^{\nu_-}$ are all well defined, it follows that the product $\gamma_R^{\nu_+} \gamma_X^{\nu_-}$ is also well defined.

We now introduce a quantity $\gamma_{R,X}$, called the *mean activity coefficient* of the electrolyte, related to γ_R and γ_X by

$$\gamma_{R,X}^{\nu_+ + \nu_-} = \gamma_R^{\nu_+} \gamma_X^{\nu_-} \qquad 8.\,10.\,4$$

Substituting (4) into (2) we have

$$\lambda_{R,X} = (\lambda_R^{\ominus})^{\nu_+} (\lambda_X^{\ominus})^{\nu_-} m_R^{\nu_+} m_X^{\nu_-} \gamma_{R,X}^{\nu_+ + \nu_-} \qquad 8.\,10.\,5$$

Since $\gamma_{R,X}$ is well defined, while γ_R and γ_X individually are not, it would be wrong to regard (4) as a definition of $\gamma_{R,X}$ in terms of γ_R and γ_X. Nevertheless formula (4) does contain something of physical significance. For let us consider a solution containing two cations R, R' and two anions X, X' from which we can form four different electrolytes, for each of which we can write a relation of the form (4). What

these relations together tell us is that the four mean activity coefficients are not independent. We can best illustrate the point by a simple example. Let us consider the two cations Na^+, K^+ and the two anions Cl^-, NO_3^-. Then we have formally

$$\gamma_{Na,Cl}^2 = \gamma_{Na^+} \gamma_{Cl^-} \qquad 8.10.6$$

$$\gamma_{K,Cl}^2 = \gamma_{K^+} \gamma_{Cl^-} \qquad 8.10.7$$

$$\gamma_{Na,NO_3}^2 = \gamma_{Na^+} \gamma_{NO_3^-} \qquad 8.10.8$$

$$\gamma_{K,NO_3}^2 = \gamma_{K^+} \gamma_{NO_3^-} \qquad 8.10.9$$

In a given solution each of the quantities on the left of formulae (6) to (9) is well defined, while the individual factors on the right are not. But these four formulae together lead to the physically significant result

$$\frac{\gamma_{Na,Cl}}{\gamma_{K,Cl}} = \frac{\gamma_{Na,NO_3}}{\gamma_{K,NO_3}} \qquad 8.10.10$$

§ 8.11 TEMPERATURE DEPENDENCE

Just as for non-ionic species, we have according to (6.05.4)

$$\frac{\partial \ln \lambda_i}{\partial T} = -\frac{H_i}{RT^2} \qquad 8.11.1$$

so that according to (8.09.1)

$$\frac{\partial \ln (\lambda_i^\ominus \gamma_i)}{\partial T} = -\frac{H_i}{RT^2} \qquad 8.11.2$$

Proceeding to the limit of infinite dilution (2) becomes

$$\frac{\partial \ln \lambda_i^\ominus}{\partial T} = -\frac{H_i^\circ}{RT^2} \qquad 8.11.3$$

where the superscript ∞ denotes the limiting value when $\Sigma_i m_i \to 0$. Now subtracting (3) from (2) we find

$$\frac{\partial \ln \gamma_i}{\partial T} = -\frac{H_i - H_i^\infty}{RT^2} \qquad 8.11.4$$

For reasons previously given, only linear combinations of these formulae will occur of the type defined by (8.04.18). In particular

for an electrolyte composed of ν_+ cations R and ν_- anions X, we have according to (1)

$$\frac{\partial \ln \lambda_{R,X}}{\partial T} = -\frac{H_{R,X}}{RT^2} \qquad 8.\,11.\,5$$

where

$$H_{R,X} = \nu_+ H_R + \nu_- H_X \qquad 8.\,11.\,6$$

is the *partial molar heat function* of the electrolyte. Similarly from (4) we deduce

$$(\nu_+ + \nu_-)\frac{\partial \ln \gamma_{R,X}}{\partial T} = -\frac{H_{R,X} - H_{R,X}^\infty}{RT^2} \qquad 8.\,11.\,7$$

where $H_{R,X}^\infty$ denotes the limiting value of $H_{R,X}$ as $\Sigma_i\, m_i \to 0$.

§ 8. 12 DISTRIBUTION OF ELECTROLYTE BETWEEN TWO SOLVENTS

The equilibrium condition for the distribution of an electrolyte consisting of ν_+ cations R and ν_- anions X between two solvents α and β can be written either in terms of the electrolytes as

$$\lambda_{R,X}^\alpha = \lambda_{R,X}^\beta \qquad 8.\,12.\,1$$

or in terms of the ions as

$$(\lambda_R^\alpha)^{\nu_+}(\lambda_X^\alpha)^{\nu_-} = (\lambda_R^\beta)^{\nu_+}(\lambda_X^\beta)^{\nu_-} \qquad 8.\,12.\,2$$

According to (8. 10. 1) the two conditions are equivalent. Substituting (8. 10. 5) into (1) we obtain

$$\frac{[m_R^{\nu_+} m_X^{\nu_-} \gamma_{R,X}^{\nu_+ + \nu_-}]^\beta}{[m_R^{\nu_+} m_X^{\nu_-} \gamma_{R,X}^{\nu_+ + \nu_-}]^\alpha} = l_{R,X}^{\alpha\beta} \qquad 8.\,12.\,3$$

where

$$l_{R,X}^{\alpha\beta} = \left(\frac{\lambda_R^{\ominus\alpha}}{\lambda_R^{\ominus\beta}}\right)^{\nu_+}\left(\frac{\lambda_X^{\ominus\alpha}}{\lambda_X^{\ominus\beta}}\right)^{\nu_-} \qquad 8.\,12.\,4$$

and according to (8. 11. 3) we have

$$\frac{\partial \ln l_{R,X}^{\alpha\beta}}{\partial T} = \frac{H_{R,X}^{\infty\beta} - H_{R,X}^{\infty\alpha}}{RT^2} \qquad 8.\,12.\,5$$

We notice that the numerator of the right side is the limiting value as $\Sigma_i\, m_i \to 0$ of the *partial molar heat of transfer of the electrolyte* from the solvent α to the solvent β.

§ 8. 13 SOLUBILITY PRODUCT

For the equilibrium between the solid electrolyte composed of the ions R, X and a solution containing R, X and possibly other electrolytes, we have

$$\lambda_{R,X} = \lambda^S_{R,X} \qquad 8.\,13.\,1$$

where we denote the solid phase by the superscript ^{S} and the solution by no superscript.

Substituting from (8. 10. 5) into (1) we obtain

$$m^{\nu_+}_R \, m^{\nu_-}_X \, \gamma^{\nu_++\nu_-}_{R,X} = s^{\nu_++\nu_-}_{R,X} \qquad 8.\,13.\,2$$

where

$$s^{\nu_++\nu_-}_{R,X} = \frac{\lambda^S_{R,X}}{(\lambda^\ominus_R)^{\nu_+}(\lambda^\ominus_X)^{\nu_-}} \qquad 8.\,13.\,3$$

is called the *solubility product* of the electrolyte and $s_{R,X}$ is called the *mean solubility* of the electrolyte. Since

$$\frac{\partial \ln \lambda^S_{R,X}}{\partial T} = -\frac{H^S_{R,X}}{RT^2} \qquad 8.\,13.\,4$$

we have, using this and (8. 11. 3) in (3)

$$\frac{\partial \ln s_{R,X}}{\partial T} = \frac{H^\infty_{R,X} - H^S_{R,X}}{(\nu_+ + \nu_-)\,RT^2} \qquad 8.\,13.\,5$$

We notice that the numerator on the right of (5) is the limiting value as $\Sigma_i m_i \to 0$ of the *heat of solution of the solid electrolyte* in the given solvent.

§ 8. 14 CHEMICAL REACTIONS

If we consider the chemical reaction

$$\Sigma \, \nu_A \, A \to \Sigma \, \nu_B \, B \qquad 8.\,14.\,1$$

where some or all of the species A, B may be ionic, the condition of equilibrium, in the notation defined in § 7. 01 is according to (7. 16. 3)

$$\Pi \, (m_i) \, \Pi \, (\gamma_i) = K_m \, (T) \qquad 8.\,14.\,2$$

The fact that some or all of the reacting species may be ions has no effect on the form of (2). It is however of interest to notice that, owing

to the conservation of net electric charge, it follows from (1) that

$$\Sigma \, \nu_A z_A = \Sigma \, \nu_B z_B \qquad 8.\,14.\,3$$

and so

$$\Pi \, (\gamma_i) = \frac{(\gamma_B)^{\nu_B}}{(\gamma_A)^{\nu_A}} \qquad 8.\,14.\,4$$

conforms to the type of product which is physically well defined according to the condition (8. 04. 18).

We shall illustrate the point by an example. Consider the reaction

$$2Fe^{3+} + Sn^{2+} \rightarrow 2Fe^{2+} + Sn^{4+} \qquad 8.\,14.\,5$$
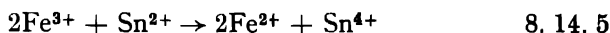
According to (2) the equilibrium condition is

$$\frac{m_{Fe^{2+}}^2 \; m_{Sn^{4+}}}{m_{Fe^{3+}}^2 \; m_{Sn^{2+}}} \; \frac{\gamma_{Fe^{2+}}^2 \gamma_{Sn^{4+}}}{\gamma_{Fe^{3+}}^2 \gamma_{Sn^{2+}}} = K_m \qquad 8.\,14.\,6$$

wherein the *activity coefficients quotient* is well defined. It can in fact be expressed in terms of mean activity coefficients as follows

$$\frac{\gamma_{Fe^{2+}}^2 \gamma_{Sn^{4+}}}{\gamma_{Fe^{3+}}^2 \gamma_{Sn^{2+}}} = \frac{\gamma_{Fe^{2+}}^2 \gamma_{Sn^{4+}} \gamma_{Cl^-}^8}{\gamma_{Fe^{3+}}^2 \gamma_{Sn^{2+}} \gamma_{Cl^-}^8} = \frac{\gamma_{Fe^{2+},Cl^-}^6 \; \gamma_{Sn^{4+},Cl^-}^5}{\gamma_{Fe^{3+},Cl^-}^8 \; \gamma_{Sn^{2+},Cl^-}^3} \qquad 8.\,14.\,7$$

For the temperature dependence of K_m we have (7. 17. 2)

$$\frac{\partial \ln K_m}{\partial T} = \frac{\Delta H^\circ}{RT^2} \qquad 8.\,14.\,8$$

where ΔH^∞ denotes the *heat of reaction* at infinite dilution.

§ 8. 15 GIBBS-DUHEM RELATION FOR ELECTROLYTE SOLUTIONS

For any phase whatever we have the Gibbs-Duhem relation (1. 38. 2). For a solution of electrolytes in a solvent 1 this becomes

$$SdT - VdP + n_1 \, d\mu_1 + \Sigma_i \, n_i \, d\mu_i = 0 \qquad 8.\,15.\,1$$

or considering variations of composition at constant temperature and pressure

$$n_1 \, D\mu_1 + \Sigma_i \, n_i \, D\mu_i = 0 \qquad 8.\,15.\,2$$

in the notation described in § 5. 03. We may rewrite (2) in terms of absolute activities λ_i as

$$n_1 \, D \ln \lambda_1 + \Sigma_i \, n_i \, D \ln \lambda_i = 0 \qquad 8.\,15.\,3$$

According to the definition of mole ratios and molalities given in § 6. 02 and extended to ions in § 8. 02 we have

$$r_i = M_1 m_i = \frac{n_i}{n_1} \qquad \text{8. 15. 4}$$

If then we divide (2) and (3) throughout by n_1 and use (4) we obtain

$$D\mu_1 = -\Sigma_i r_i D\mu_i = -M_1 \Sigma_i m_i D\mu_i \qquad \text{8. 15. 5}$$

$$D \ln \lambda_1 = -\Sigma_i r_i D \ln \lambda_i = -M_1 \Sigma_i m_i D \ln \lambda_i \qquad \text{8.15. 6}$$

As explained in § 8. 03 all variations of composition of an electrolyte solution are subject to the condition for electrical neutrality

$$\Sigma_i z_i m_i = 0 \qquad \text{8. 15. 7}$$

so that

$$\Sigma_i z_i \, dm_i = 0 \qquad \text{8. 15. 8}$$

The variations in formulae (1), (2), (3), (5), (6) are all subject to the condition (8): but for variations satisfying (8) these formulae hold just as well for electrolyte solutions as for any other solutions.

We now recall the definition of the osmotic coefficient by (8. 06. 1)

$$\ln \frac{\lambda_1}{\lambda_1^0} = -\varphi \Sigma_i r_i = -\varphi M_1 \Sigma_i m_i \qquad \text{8. 15. 9}$$

and the definition of ionic activity coefficients γ_i by (8. 09. 1)

$$\lambda_i = \lambda_i^\ominus m_i \gamma_i \qquad \text{8. 15. 10}$$

Differentiating (9) with respect to changes of composition at constant temperature we obtain

$$D \ln \lambda_1 = -M_1 D \left(\varphi \Sigma_i m_i\right) \qquad \text{8. 15. 11}$$

Taking logarithms of (10) and similarly differentiating we obtain

$$D \ln \lambda_i = \frac{Dm_i}{m_i} + D \ln \gamma_i \qquad \text{8. 15. 12}$$

Now substituting (11) and (12) into (6) we obtain

$$D \left\{ (\varphi - 1) \Sigma_i m_i \right\} = \Sigma_i m_i D \ln \gamma_i \qquad \text{8. 15. 13}$$

of the same form as formula (6. 13. 2).

In particular for a solution of a single electrolyte having ν_+ cations R and ν_- anions X, formula (13) becomes

$$(\nu_+ + \nu_-) \frac{\partial}{\partial m} \{(1 - \varphi) \, m\} = - \nu_+ m \frac{\partial \ln \gamma_R}{\partial m} - \nu_- m \frac{\partial \ln \gamma_X}{\partial m} \qquad 8.\,15.\,14$$

where m denotes the *molality of the electrolyte*. The mean activity coefficient $\gamma_{R,X}$ of the electrolyte is related to the ionic activity coefficients γ_R and γ_X by (8. 10. 4)

$$\gamma_{R\,X}^{\nu_+ + \nu_-} = \gamma_R^{\nu_+} \gamma_X^{\nu_-} \qquad 8.\,15.\,15$$

We now divide (14) throughout by $(\nu_+ + \nu_-) \, m$ and use (15) obtaining

$$- \frac{\partial \ln \gamma_{R,X}}{\partial m} = \frac{1}{m} \frac{\partial}{\partial m} \{(1 - \varphi) \, m\} \qquad 8.\,15.\,16$$

or integrating from 0 to m

$$- \ln \gamma_{R,X} = \int_0^m \frac{\partial \{(1 - \varphi) \, m\}}{\partial m} \frac{\mathrm{d}m}{m} \qquad 8.\,15.\,17$$

Just as in a solution of a single solute non-electrolyte, formula (16) or (17) may be used to determine either of the quantities γ or φ if the other is known as a function of composition at all molalities less than m. On the other hand the more general relation (13) should not be used in this manner, but rather as a check on the self-consistency of assumed formulae for φ and the γ_i's, because it is also necessary for the γ_i's to satisfy the relations of the type

$$\frac{\partial \ln \gamma_i}{\partial m_k} = \frac{\partial \ln \gamma_k}{\partial m_i} \qquad 8.\,15.\,18$$

As an example of (17) suppose

$$1 - \varphi = a m^t \qquad (a, t \text{ const.}) \qquad 8.\,15.\,19$$

Then substituting (19) into (17) we obtain

$$- \ln \gamma_{R,X} = \left(\frac{t+1}{t}\right) a m^t = \left(\frac{t+1}{t}\right) (1 - \varphi) \qquad 8.\,15.\,20$$

§ 8. 16 LIMITING LAW AT HIGH DILUTIONS

It was already proved * over forty years ago that deviations from ideality due to the long range electrostatic interactions between ions

* Milner, *Phil. Mag.* 1912 **23** 551.

in highly dilute electrolyte solutions are quite different from the deviations in nonelectrolyte solutions.

The distinction can for a single solute be expressed in the form

$$1 - \varphi \propto m \quad \text{as} \quad m \to 0 \qquad \text{(non-electrolyte)} \qquad 8.\,16.\,1$$

$$1 - \varphi \propto m^t \quad \text{as} \quad m \to 0 \quad (t < 1) \quad \text{(electrolyte)} \qquad 8.\,16.\,2$$

This distinction is most strikingly expressed in the form

$$\frac{d\,(1 - \varphi)}{dm} \to \text{finite limit as } m \to 0 \text{ (non-electrolyte)} \qquad 8.\,16.\,3$$

$$\frac{d\,(1 - \varphi)}{dm} \to \infty \text{ as } m \to 0 \qquad \text{(electrolyte)} \qquad 8.\,16.\,4$$

The latter behaviour is shown graphically in fig. 8. 1 which is of
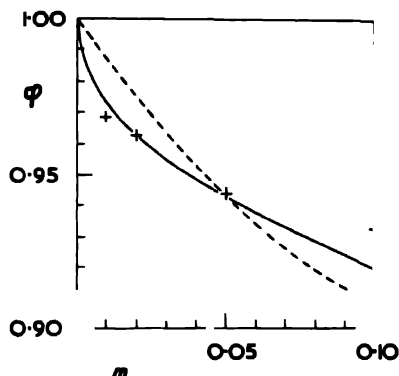
Fig. 8. 1. + + Freezing-point measurements.
——— Electrostatic interaction according to Milner.
- - - - Incomplete dissociation ignoring electrostatic interaction.

historical interest being taken from a paper by Bjerrum * written as early as 1916.

Milner † in 1912 had shown by statistical methods that the theoretical value of t is near $\frac{1}{2}$.

Various values of t in (2) were used empirically among which the value $t = \frac{1}{2}$ was used by Brönsted ‡ in the period around 1922.

Finally in 1923 Debye and Hückel§ determined by a statistical

* Bjerrum, 16te Skand. Naturforskermöte 1916 p. 229.
† Milner, *Phil. Mag.* 1912 **23** 551.
‡ Brönsted, *J. Amer. Chem. Soc.* 1922 **44** 938.
§ Debye and Hückel, *Phys. Z.* 1923 **24** 185.

treatment the theoretical law valid in the limit $m \to 0$. According to this law $t = \frac{1}{2}$ and the proportionality constant in (2) is also determined by the theory.

§ 8. 17 LIMITING LAW FOR SINGLE ELECTROLYTE

For a single electrolyte having ν_+ positive ions with charge number z_+ and ν_- negative ions with charge number z_-, satisfying the condition of electrical neutrality $\nu_+ z_+ + \nu_- z_- = 0$, Debye's limiting law valid as $m \to 0$ takes the form

$$1 - \varphi = \frac{1}{3} a z_+ |z_-| \left(\frac{\nu_+ z_+^2 + \nu_- z_-^2}{2} \right)^{\frac{1}{2}} m^{\frac{1}{2}} \qquad 8.\,17.\,1$$

The coefficient a depends only on the solvent and temperature and is given by

$$\tfrac{1}{3} a = \left(\frac{2\pi L \varrho}{9} \right)^{\frac{1}{2}} \left(\frac{e^2}{\varepsilon k T} \right)^{\frac{3}{2}} \qquad 8.\,17.\,2$$

where L denotes Avogadro's number, k Boltzmann's constant, e the charge of a proton, ϱ the density of the solvent, and ε the permittivity of the solvent.

For example for water at 0 °C we have

$L = 0.6024 \times 10^{24}$ mole^{-1}
$\varrho = 0.9999 \times 10^{-3}$ kg cm^{-3}
$e = 4.803 \times 10^{-10}$ franklin *
$\varepsilon = 88.23$ franklin^2 erg^{-1} cm^{-1}
$k = 1.380 \times 10^{-16}$ erg deg^{-1}
$T = 273.15$ deg

Inserting these values into (2) we obtain

$$\tfrac{1}{3} a = 0.374 \text{ kg}^{\frac{1}{2}} \text{ mole}^{-\frac{1}{2}} \qquad \text{(water at 0 °C)} \qquad 8.\,17.\,3$$

For the mean activity coefficient of the electrolyte, since (1) is of the form (8. 15. 19) with $t = \frac{1}{2}$, we may use (8. 15. 20) so that

$$- \ln \gamma_{R,X} = 3 (1 - \varphi)$$

$$= a z_+ |z_-| \left(\frac{\nu_+ z_+^2 + \nu_- z_-^2}{2} \right)^{\frac{1}{2}} m^{\frac{1}{2}} \qquad 8.\,17.\,4$$

* The name *franklin* is used for a charge which repels a similar charge at a distance one centimetre in vacuo with a force of one dyne. See *Nature* 1941 **148** 751.

In particular for water at 0 °C

$$a = 1.124 \text{ kg}^{\frac{1}{2}} \text{ mole}^{-\frac{1}{2}}$$

$$a/\ln 10 = 0.488 \text{ kg}^{\frac{1}{2}} \text{ mole}^{-\frac{1}{2}} \qquad 8.17.5$$

For water at 25 °C the values of the coefficients are

$$a = 1.171 \text{ kg}^{\frac{1}{2}} \text{ mole}^{-\frac{1}{2}}$$

$$a/\ln 10 = 0.5085 \text{ kg}^{\frac{1}{2}} \text{ mole}^{-\frac{1}{2}} \qquad 8.17.6$$

§ 8.18 IONIC STRENGTH

The *ionic strength* I of an electrolyte solution is defined, following Lewis and Randall *, by

$$I = \tfrac{1}{2} \Sigma_i z_i^2 m_i \qquad 8.18.1$$

so that in the case of a single solute electrolyte at a molality m

$$I = \tfrac{1}{2}(\nu_+ z_+^2 + \nu_- z_-^2) \, m \qquad 8.18.2$$

Using (2) we can write the formulae of the previous section in the shorter forms

$$1 - \varphi = \tfrac{1}{3} \, a \, z_+|z_-|I^{\frac{1}{2}} \qquad 8.18.3$$

$$- \ln \gamma_{R,X} = a z_+|z_-|I^{\frac{1}{2}} \qquad 8.18.4$$

According to the limiting law (3) if $(1 - \varphi)/z_+ z_-$ is plotted against $I^{\frac{1}{2}}$ for electrolytes of various electric charge types, we should obtain a sheaf of curves all having the same initial slope equal to $-a/3$. This is shown in fig. 8.2 for several typical electrolytes at 0 °C. The experimental curves have been determined by freezing point measurements and the initial slope of each as drawn is equal to the theoretical value given by (8.17.3).

§ 8.19 LIMITING LAW FOR MIXED ELECTROLYTES

Debye's limiting law as $\Sigma_i m_i \to 0$ for a solution containing more than one electrolyte can be expressed as follows. If G denotes the Gibbs function of the actual solution while G^{id} denotes the same function for an ideal dilute solution of the same composition, then

$$\frac{G - G^{\text{id}}}{RT} = - \tfrac{2}{3} a \frac{(\Sigma_i z_i^2 n_i)^{\frac{3}{2}}}{(2 n_1 M_1)^{\frac{1}{2}}} \qquad 8.19.1$$

where a is defined by (8.17.2).

* Lewis and Randall, *J. Amer. Chem. Soc.* 1921 **43** 1141.

$10^2 I/\text{mole kg}^{-1}$
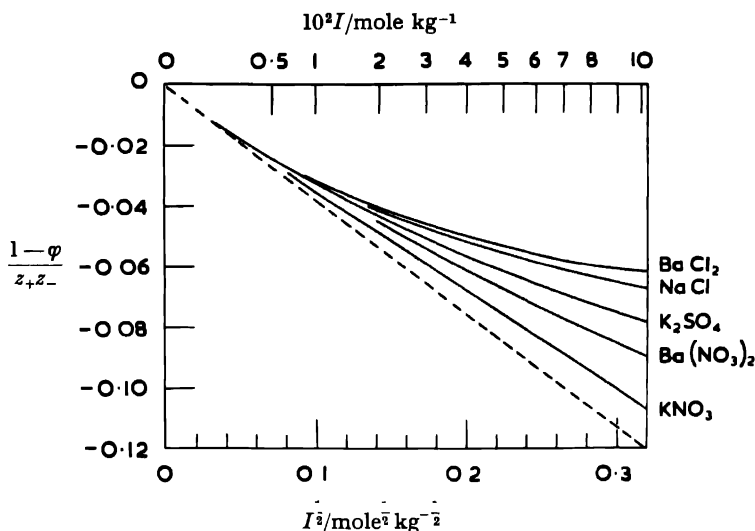
Fig. 8. 2. Osmotic coefficients of electrolytes of various charge types at 0 °C.

By differentiation of (1) with respect to n_i, we obtain using (8. 02. 2) and (8. 18. 1)

$$-\ln \gamma_i = -\frac{1}{RT}\frac{\partial(G-G^{\text{id}})}{\partial n_i} = az_i^2\left(\frac{\Sigma_i z_i^2 n_i}{2n_1 M_1}\right)^{\frac{1}{2}}$$

$$= az_i^2\left(\frac{\Sigma_i z_i^2 m_i}{2}\right)^{\frac{1}{2}} = az_i^2 I^{\frac{1}{2}} \qquad 8.\ 19.\ 2$$

Consequently for the mean activity coefficient of an electrolyte composed of ν_+ cations R of charge number z_+ and ν_- anions X of charge number z_-, we have

$$-\ln \gamma_{R,X} = -\frac{\nu_+ \ln \gamma_R + \nu_- \ln \gamma_X}{\nu_+ + \nu_-}$$

$$= -\frac{\nu_+ z_+^2 + \nu_- z_-^2}{\nu_+ + \nu_-}\, aI^{\frac{1}{2}}$$

$$= az_+|z_-|I^{\frac{1}{2}} \qquad 8.\ 19.\ 3$$

using the condition of electrical neutrality

$$\nu_+ z_+ + \nu_- z_- = 0 \qquad 8.\ 19.\ 4$$

From (3) we see that in the limit of high dilutions the mean activity coefficient of a given electrolyte has the same value in different solu-

tions of the same ionic strength. This principle, which follows from Debye's formula, was discovered experimentally by Lewis and Randall * in 1921. Our previous formula (8. 18. 4) for a solution containing only one electrolyte is a special case of (8. 19. 3).

By differentiating (1) with respect to n_1 we obtain

$$\frac{\mu_1 - \mu_1^{\text{id}}}{RT} = \ln \frac{\lambda_1}{\lambda_1^{\text{id}}} = \tfrac{1}{3} a \frac{(\Sigma_i z_i^2 n_i)^{\frac{3}{2}}}{(2M_1)^{\frac{1}{2}} n_1^{\frac{3}{2}}}$$

8. 19. 5

where the superscript ${}^{\text{id}}$ denotes the value in an ideal dilute solution having the same composition as the actual solution. Using this notation, we obtain from (8. 06. 1)

$$\ln \frac{\lambda_1}{\lambda_1^{\text{id}}} = (1 - \varphi) M_1 \Sigma_i m_i$$

8. 19. 6

Comparing (5) and (6) we have

$$1 - \varphi = \tfrac{1}{3} a \frac{(\Sigma_i z_i^2 n_i)^{\frac{3}{2}}}{2^{\frac{1}{2}} (M_1 n_1)^{\frac{3}{2}} \Sigma_i m_i}$$

$$= \tfrac{1}{3} a \frac{(\Sigma_i z_i^2 m_i)^{\frac{3}{2}}}{2^{\frac{1}{2}} \Sigma_i m_i}$$

$$= \tfrac{1}{3} a \frac{\Sigma_i z_i^2 m_i}{\Sigma_i m_i} I^{\frac{1}{2}}$$

8. 19. 7

In the special case of a single electrolyte formula (7), by use of the condition of electrical neutrality, reduces to (8. 18. 3).

Since formulae (2) and (7) are both derived from (1) they automatically satisfy the Gibbs-Duhem relation and the relations (8. 15. 18).

§ 8. 20 LESS DILUTE SOLUTIONS

The limiting law of Debye described in the previous three sections is of the greatest value in providing a reliable means of extrapolating experimental data to infinite dilution, since experimental measurements determine only ratios of the values of γ in the several solutions. To determine values of γ itself in the several solutions some assumption has to be made concerning the value of γ in at least one such solution, for example the most dilute. Debye's limiting law provides the necessary assumption.

On the other hand this limiting law is accurate only at very high

* Lewis and Randall, *J. Amer. Chem. Soc.* 1921 **43** 1141.

dilutions. For example when the solvent is water it is accurate at $I = 10^{-3}$ mole kg^{-1}, but already at $I = 10^{-2}$ mole kg^{-1} deviations are experimentally detectable and at $I = 10^{-1}$ mole kg^{-1} deviations are serious. In other solvents having smaller permittivities deviations from the limiting law appear at correspondingly lower ionic strengths.

For less dilute solutions various formulae can be used, all reducing to the limiting formula of Debye at high dilutions and all more or less empirical at less high dilutions. Some of these will be described in the succeeding sections.

§ 8. 21 SINGLE ELECTROLYTES

The simplest formula for the activity coefficient of a single electrolyte, which conforms with Debye's limiting formula, is

$$\ln \gamma_{\mathrm{R,X}} = - a z_+ |z_-| I^{\frac{1}{2}} + 2\beta_{\mathrm{R,X}}\, m \qquad 8.\,21.\,1$$

where a is defined by (8. 17. 2) and $\beta_{\mathrm{R,X}}$ depends on the solvent, the solute and the temperature but not on the molality. This type of formula was used by Brönsted * as early as 1921 for uni-univalent electrolytes with a value for a about 20 % lower than the value established theoretically two years later. The objection to this formula is its limited range of validity, since it ceases to represent the experimental data at ionic strengths appreciably less than 0.1 mole kg^{-1} in water.

A theoretical formula due to Debye and Hückel † is

$$\ln \gamma_{\mathrm{R,X}} = - a z_+ |z_-| \frac{I^{\frac{1}{2}}}{1 + \varrho_{\mathrm{R,X}} I^{\frac{1}{2}}} \qquad 8.\,21.\,2$$

where $\varrho_{\mathrm{R,X}}$ is a parameter independent of I. According to a model in which the cations and anions are treated as rigid non-polarizable spheres of equal size $\varrho_{\mathrm{R,X}}$ is directly proportional to the diameter of these spheres. Alternatively we may more safely regard $\varrho_{\mathrm{R,X}}$ as an empirical parameter. By suitable choice of values for $\varrho_{\mathrm{R,X}}$ formula (2) can represent the experimental data in water at ionic strengths up to 0.1 mole kg^{-1} or even higher. The objection to (2) is that it cannot be readily extended to solutions containing more than one electrolyte.

A formula proposed by Hückel ‡ is

* Brönsted, *J. Amer. Chem. Soc.* 1922 **44** 938.
† Debye and Hückel, *Phys. Z.* 1923 **24** 185.
‡ Hückel, *Phys. Z.* 1925 **26** 93.

$$\ln \gamma_{R,X} = - az_+|z_-| \frac{I^{\frac{1}{2}}}{1 + \varrho_{R,X} I^{\frac{1}{2}}} + 2\beta_{R,X} m \qquad 8.\,21.\,3$$

where, in spite of what Hückel may have thought to the contrary, $\beta_{R,X}$ is another empirical parameter. Since formula (3) contains two adjustable parameters $\varrho_{R,X}$ and $\beta_{R,X}$ it can be made to fit the experimental data up to much higher ionic strengths than either (1) or (2). For solutions in water formula (3) can remain accurate up to $I = 1$ mole kg^{-1}. The objection to (3) is the same as to (2), namely the impossibility of its extension to solutions containing several electrolytes.

Güntelberg * suggested the use of the formula

$$\ln \gamma_{R,X} = - az_+|z_-| \frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} \qquad 8.\,21.\,4$$

containing no adjustable parameter. Obviously such a formula cannot compete in accuracy with formulae such as (1) and (2) containing an adjustable parameter, much less with (3) containing two such parameters. Nevertheless Güntelberg's formula gives a useful representation of the average behaviour of many electrolytes in water up to $I = 0.1$ mole kg^{-1}. In the absence of experimental data it is as good an approximation as any other guess. This formula has moreover the advantage over (2) and (3) that it can be extended to solutions of several electrolytes.

Finally we mention a formula proposed by the author †

$$\ln \gamma_{R,X} = - az_+|z_-| \frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} + 2\beta_{R,X} \tilde{\nu} m \qquad 8.\,21.\,5$$

where $\tilde{\nu}$ is the harmonic mean of ν_+ and ν_-, that is

$$\frac{2}{\tilde{\nu}} = \frac{1}{\nu_+} + \frac{1}{\nu_-} \qquad 8.\,21.\,6$$

This formula combines the advantages of Brönsted's formula (1) and Güntelberg's formula (4). Containing one adjustable parameter $\beta_{R,X}$ it is accurate for solutions in water up to $I = 0.1$ mole kg^{-1}. It has the advantage over Debye's formula (2) and Hückel's formula (3), that, as we shall describe in the next section, it can be readily extended to solutions of several electrolytes. The constant factor $2\tilde{\nu}$ has been included for convenience, as we shall see later.

* Güntelberg, *Z. phys. Chem.* 1926 **123** 243.

† Guggenheim, *Phil. Mag.* 1935 **19** 588.

§ 8. 22 SEVERAL ELECTROLYTES

For solutions containing more than one electrolyte we propose * the following extension of the limiting law (8. 19. 1)

$$\frac{G - G^{\mathrm{id}}}{RT} = -\tfrac{2}{3}a \frac{(\Sigma_R z_R^2 n_R + \Sigma_X z_X^2 n_X)^{\frac{3}{2}}}{(2n_1 M_1)^{\frac{1}{2}}} \tau(I^{\frac{1}{2}})$$

$$+ \Sigma_R \Sigma_X \frac{2\beta_{R,X} n_R n_X}{n_1 M_1} \qquad\qquad 8. 22. 1$$

where R denotes cations, X denotes anions and $\tau(I^{\frac{1}{2}})$ is a function of $I^{\frac{1}{2}}$ defined by

$$\tau(y) = \frac{3}{y^3} \{\ln(1 + y) - y + \tfrac{1}{2}y^2\}$$

$$= 1 - \tfrac{3}{4}y + \tfrac{3}{5}y^2 - \tfrac{3}{6}y^3 + \tfrac{3}{7}y^4 - \ldots \qquad 8. 22. 2$$

Differentiating (1) with respect to n_R we obtain using (8. 02. 2) and (8. 18. 1)

$$\ln \gamma_R = -az_R^2 \frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} + 2\Sigma_{X'} \beta_{R,X'} m_{X'} \qquad 8. 22. 3$$

and similarly

$$\ln \gamma_X = -az_X^2 \frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} + 2\Sigma_{R'} \beta_{R',X} m_{R'} \qquad 8. 22. 4$$

In (3) and (4) we have used R to denote a particular cation and R' to denote every cation; a similar remark applies to X and X'. From (3) and (4) we derive

$$\ln \gamma_{R,X} = -az_R|z_X| \frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} + \frac{\nu_+}{\nu_+ + \nu_-} 2\Sigma_{X'} \beta_{R,X'} m_{X'}$$

$$+ \frac{\nu_-}{\nu_+ + \nu_-} 2\Sigma_{R'} \beta_{R',X} m_{R'} \qquad 8. 22. 5$$

In the particular case of a solution containing only a single electrolyte, (5) reduces to

$$\ln \gamma_{R,X} = -az_+|z_-| \frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} + \frac{\nu_- m_R + \nu_+ m_X}{\nu_+ + \nu_-} 2\beta_{R,X} \qquad 8. 22. 6$$

* See Guggenheim, *Phil. Mag.* 1935 **19** 588.

But if m denotes the molality of the single electrolyte

$$m_R = \nu_+ m \qquad\qquad 8.22.7$$

$$m_X = \nu_- m \qquad\qquad 8.22.8$$

by the definitions of ν_+, ν_-. Hence

$$\frac{\nu_- m_R + \nu_+ m_X}{\nu_+ + \nu_-} = \frac{2\nu_+ \nu_-}{\nu_+ + \nu_-}\, m = \tilde{\nu} m \qquad\qquad 8.22.9$$

according to (8.21.6) which defines $\tilde{\nu}$. Substituting (9) into (6) we obtain

$$\ln \gamma_{R,X} = -\, az_+|z_-|\frac{I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} + 2\beta_{R,X}\,\tilde{\nu} m \qquad\qquad 8.22.10$$

in agreement with (8.21.5)

We thus see that formula (5) includes formula (8.21.5) for a single electrolyte as a special case. Moreover, since (5) was derived by differentiation of (1), the Gibbs-Duhem relation and (8.15.18) are automatically satisfied. We emphasize that an analogous extension of formula (8.21.2) containing different parameters $\varrho_{R,X}$ for the several electrolytes in the mixture is not possible since the relations (8.15.18) would be violated.

By differentiating (1) with respect to n_1 and using (8.19.6) we can obtain a formula for the osmotic coefficient φ. For the sake of brevity we confine ourselves to solutions containing electrolytes all of the same charge type such that each is composed of ν_+ cations of charge number z_+ and ν_- anions of charge number z_-, satisfying

$$\nu_+ z_+ + \nu_- z_- = 0 \qquad\qquad 8.22.11$$

We then obtain

$$\varphi - 1 = -\tfrac{1}{3}az_+|z_-|I^{\frac{1}{2}}\,\sigma\,(I^{\frac{1}{2}}) + \frac{2\,\Sigma_R\,\Sigma_X\,\beta_{R,X}\,m_R\,m_X}{\Sigma_R\,m_R + \Sigma_X\,m_X} \qquad\qquad 8.22.12$$

where $\sigma(I^{\frac{1}{2}})$ is a function of $I^{\frac{1}{2}}$ defined by

$$\sigma(y) = \frac{3}{y^3}\left\{ 1 + y - \frac{1}{1+y} - 2\ln(1+y) \right\}$$

$$= 1 - 3\left\{ \tfrac{2}{4}y - \tfrac{3}{5}y^2 + \tfrac{4}{6}y^3 - \tfrac{5}{7}y^4 + \ldots \right\} \qquad\qquad 8.22.13$$

In particular for a solution of a single electrolyte

$$1 - \varphi = \tfrac{1}{3}az_+|z_-|I^{\frac{1}{2}}\sigma(I^{\frac{1}{2}}) - \beta_{R,X}\tilde{\nu} m \qquad\qquad 8.22.14$$

We may note that the functions τ and σ defined by (2) and (13) respectively are related by the identity

$$2\tau(y) + \sigma(y) = \frac{3}{1 + y} \qquad\qquad 8.\,22.\,15$$

§ 8. 23 SPECIFIC INTERACTION OF IONS

If we examine formula (8. 22. 1) from which all subsequent formulae for γ's and φ are derived, we notice that there is a parameter $\beta_{R,X}$ for each cation-anion pair, but no such parameters $\beta_{R,R'}$ or $\beta_{X,X'}$ belonging to two ions with electric charge of the same sign. This is in accordance with a principle enunciated by Brönsted * in 1921 and called by him *the principle of specific interaction of ions*. According to this principle two ions of the same sign will so rarely come close to each other in dilute solution that their mutual interactions may be assumed to be determined by their charges, but otherwise to be non-specific. Ions of the opposite sign on the other hand often come close to each other and their mutual interactions are therefore specific depending on their sizes, shapes, polarizabilities and so on. When this principle is introduced into a statistical treatment † it leads to parameters of the type $\beta_{R,X}$ but none of the type $\beta_{R,R'}$ or $\beta_{X,X'}$.

§ 8. 24 COMPARISON WITH EXPERIMENT

The *principle of specific interaction* leads to a number of conclusions concerning mixtures of electrolytes which have been confirmed experimentally by Brönsted *. We shall not give details, but shall merely mention one illustrative example of the usefulness of the principle.

From formula (8. 22. 5) it follows that the mean activity of NaCl present as a trace in a solution of HCl at $m = 10^{-1}$ mole kg^{-1} is equal to that of HCl present as a trace in a solution of NaCl at $m = 10^{-1}$ mole kg^{-1}. The latter can be measured electrometrically, as we shall see in the next chapter, while there is no convenient experimental method for determining the former. Hence the former is best determined by measuring the latter.

Values of the parameter $\beta_{R,X}$ have been determined for a large number of 1 — 1 electrolytes and for a few electrolytes of higher charge

* Brönsted, *Kgl. Danske Vid. Selsk. Math.-fys. Medd.* 1921 **4** (4); *J. Amer. Chem. Soc.* 1922 **44** 877; 1923 **45** 2898.

† See Guꞯenheim, *Kgl. Danske Vid. Selsk. Math.-fys. Medd.* 1955 **30** (1).

type. A list of such values * is given in table 8. 1. The values at 0 °C are obtained from freezing-point measurements, especially those of Scatchard and his collaborators. Most of these are probably accurate to better than $\pm$ 0.02 kg mole^{-1}. The values at 25 °C for HCl, NaCl and KCl are obtained from electromotive force measurements by use of the theory given in the following chapter. These values are probably, also accurate to $\pm$ 0.02 kg mole^{-1}. The remaining values at 25 °C are obtained by the isopiestic measurements relative to NaCl or KCl of Robinson and Stokes. Some of these may be uncertain by as much as $\pm$ 0.1 but most of them are probably more accurate than this.

TABLE 8. 1 —β values

electrolyte	0 °C $\dfrac{\beta}{\text{kg mole}^{-1}}$	25 °C $\dfrac{\beta}{\text{kg mole}^{-1}}$	electrolyte	0 °C $\dfrac{\beta}{\text{kg mole}^{-1}}$	25 °C $\dfrac{\beta}{\text{kg mole}^-}$
HCl	0 25	0.27	KI		0 15
HBr		0.33	KClO$_3$	—0.2	—0.04
HI		0 36	KClO$_4$	—0 55	
HClO$_4$		0 30	KBrO$_3$		—0 07
HNO$_3$	0 16		KIO$_3$	—0 43	—0 07
LiCl	0.20	0 22	KNO$_3$	—0.30	—0 11
LiBr	0.30	0.26	KO$_2$CH	0 15	
LiI		0 35	KOAc	0 30	0.26
LiClO$_3$	0 25		KCNS		0 09
LiClO$_4$	0.35	0.34	KH$_2$PO$_4$		—0.16
LiNO$_3$	0.23	0 21	RbCl		0.06
LiO$_2$CH	0.11		RbBr		0.05
LiOAc	0.19	0.18	RbI		0.04
NaF		0.07	RbNO$_3$		—0.14
NaCl	0.11	0 15	RbOAc		0 26
NaBr	0.20	0.17	CsCl		0
NaI		0 21	CsBr		0
NaClO$_3$	0	0.10	CsI		—0 01
NaClO$_4$	0.05	0.13	CsNO$_3$		—0.15
NaBrO$_3$		0.01	CsOAc		0.28
NaIO$_3$	—0.41		AgNO$_3$		—0.14
NaNO$_3$	—0.04	0.04	TlClO$_4$		—0.17
NaO$_2$CH	0.13		TlNO$_3$		—0.36
NaOAc	0.26	0.23	TlOAc	—	—0.04
NaCNS		0.20			
NaH$_2$PO$_4$		—0.06	BaCl$_2$		+0.7
KF	0.05	0.13	Ba(NO$_3$)$_2$		—0.5
KCl	0.04	0.10	CoCl$_2$		+1.1
KBr	0.06	0.11	K$_2$SO$_4$		—0.1

* Guggenheim and Turgeon, *Trans. Faraday Soc* 1955 **51** 747.

It is worthy of note that a considerable number of electrolytes, of various charge types, have values of $\beta_{R,X}$ not greatly different from zero. Consequently if, as often happens, a value is required for the activity coefficient of some electrolyte and there are no experimental data available a useful approximation is obtained by taking $\beta_{R,X}$ as zero. This approximation, first recommended by Güntelberg, has already been mentioned in § 8. 21. It is usually a vastly better approximation than the limiting law formulae of § 8. 19. It has been suggested[*] that a more typical value for $1 - 1$ electrolytes is $2\beta_{R,X}/\ln 10 = 0.1$ kg mole^{-1} provided one excludes those electrolytes in which the extent of association to ion pairs RX is not negligible. But one can only find out which are these exceptional $1 - 1$ electrolytes by determining the value of $\beta_{R,X}$ and finding it to be negative.

§ 8. 25 ACTIVITY COEFFICIENT OF SOLVENT

We have hitherto described the equilibrium properties of the solvent by means of its osmotic coefficient φ and may thus regard $1 - \varphi$ as a measure of deviation from behaviour in an ideal dilute solution. We might alternatively have used an activity coefficient f_1 defined by

$$\frac{\lambda_1}{\lambda_1^0} = (1 - \Sigma_i \, x_i) \, f_1 \qquad\qquad 8.\ 25.\ 1$$

Let us now consider solutions so dilute that $\Sigma_i x_i \ll 1$. We may then replace (1) by the approximations

$$\ln \frac{\lambda_1^0}{\lambda_1} \simeq \Sigma_i \, x_i - \ln f_1 \simeq \Sigma_i \, r_i - \ln f_1 \qquad\qquad 8.\ 25.\ 2$$

We now compare (2) with the definition (8. 06. 1) of the osmotic coefficient φ

$$\ln \frac{\lambda_1^0}{\lambda_1} = \varphi M_1 \, \Sigma_i \, m_i = \varphi \, \Sigma_i \, r_i \qquad\qquad 8.\ 25.\ 3$$

and we obtain

$$\ln f_1 \simeq (1 - \varphi) \, \Sigma_i \, r_i \qquad\qquad 8.\ 25.\ 4$$

We now consider a typical numerical example. In a decimolal

[*] Davies, *J. Chem. Soc.* 1938, 2093.

solution of a $1 - 1$ electric charge type electrolyte in water, we have approximately

$$\Sigma_i \, r_i = 3.6 \times 10^{-3}$$
$$1 - \varphi = 0.078$$

so that

$$\ln f_1 = 2.8 \times 10^{-4}$$
$$f_1 = 1.00028$$

From this typical example we see that $f_1 - 1$ is much smaller than $1 - \varphi$ and is consequently a less convenient measure of deviation from the ideal dilute state.

It will be convenient to use the name *extremely dilute solutions* to denote solutions in which $\Sigma_i \, x_i \ll 1$. There is no implication that the deviation of such solutions from being ideal dilute is small. Nevertheless in view of the above discussion it will usually be permissible to neglect the deviation of f_1 from unity in an extremely dilute solution.

§ 8. 26 CHEMICAL REACTIONS INVOLVING SOLVENT

In § 8. 14 we obtained the condition of equilibrium in a chemical reaction between solute ionic species, including non-ionic species as if they were ionic with $z = 0$. We shall now consider how this condition can be extended to include chemical reactions involving the solvent.

A reaction involving the solvent is called *solvolysis* with the exception of simple addition called *solvation*. In particular if the solvent is water it is called *hydrolysis*.

For the sake of brevity we shall consider not the general case, but a specific example. We choose the hydrolysis of chlorine in water

$$Cl_2 + 2H_2O \rightarrow H_3O^+ + Cl^- + HClO \qquad \text{8. 26. 1}$$
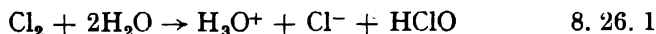
The equilibrium condition in its most general form is

$$\frac{\lambda_{H_3O^+} \, \lambda_{Cl^-} \, \lambda_{HClO}}{\lambda_{Cl_2} \, \lambda_{H_2O}^2} = 1 \qquad \text{8. 26. 2}$$

For λ_{H_2O} we may write according to (8. 25. 1)

$$\lambda_{H_2O} = \lambda_{H_2O}^0 \, (1 - \Sigma_i \, x_i) \, f_1 \qquad \text{8. 26. 3}$$

where the summation Σ_i includes the uncharged species Cl_2 and HClO as well as the ions. We saw that even for solutions far from ideal

dilute we may with a high degree of accuracy set $f_1 = 1$. Assuming the solution is *extremely dilute* so that we may further neglect $\Sigma_i x_i$ compared with unity, we may then replace (3) by

$$\lambda_{H_2O} \simeq \lambda^0_{H_2O} \qquad 8.\,26.\,4$$

with an accuracy depending on the composition of the solution, but usually within 1 %. Hence with this sort of accuracy we may replace (2) by

$$\frac{\lambda_{H_3O^+}\,\lambda_{Cl^-}\,\lambda_{HClO}}{\lambda_{Cl_2}} = \lambda^{02}_{H_2O} \qquad 8.\,26.\,5$$

Using the relation (8. 09. 1) for each reacting species other than the solvent H_2O we obtain

$$\frac{m_{H_3O^+}\,m_{Cl^-}\,m_{HClO}}{m_{Cl_2}}\;\frac{\gamma_{H_3O^+}\,\gamma_{Cl^-}\,\gamma_{HClO}}{\gamma_{Cl_2}} = K_m(T) \qquad 8.\,26.\,6$$

the constant $\lambda^{02}_{H_2O}$ being absorbed as a factor of K_m.

From this typical example we see that for a chemical reaction involving the solvent, the equilibrium condition takes the approximate form in dilute solution

$$\Pi'\,(m_i\gamma_i) = K_m(T) \qquad 8.\,26.\,7$$

where Π' differs from Π by the omission of factors relating to the solvent.

§ 8. 27 ACID-BASE EQUILIBRIUM

One of the most important classes of chemical processes between ions in solution, is that of the transfer of a proton from one ion or molecule to another. Any ion or molecule capable of losing a proton is called an *acid*; any ion or molecule capable of gaining a proton is called a *base*. These definitions due to Brönsted * are simpler and more rational than earlier definitions which they supersede. The acid and base which differ from each other by one proton are called a *conjugate* pair. Obviously the electric charge number of any acid exceeds by unity that of its conjugate base. Table 8. 2 gives examples of well known conjugate pairs of acids and bases. It is clear from several examples in table 8. 2 that an ion or a molecule may be both an acid and a base.

* Brönsted, *Rec. Trav. Chim. Pays-Bas* 1923 **42** 718.

TABLE 8. 2

Typical conjugate acids and bases

Acid	Base
CH_3CO_2H	$CH_3CO_2^-$
NH_4^+	NH_3
H_2O	OH^-
H_3O^+	H_2O
H_3PO_4	$H_2PO_4^-$
$H_2PO_4^-$	HPO_4^{2-}
HPO_4^{2-}	PO_4^{3-}
$H_3N^+.CH_2.CO_2H$	$H_3N^+.CH_2.CO_2^-$
$H_3N^+.CH_2.CO_2^-$	$H_2N.CH_2 CO_2^-$

If A and B denote an acid and its conjugate base, while A', B' denote another conjugate pair then the chemical reaction

$$A + B' \rightarrow B + A' \qquad 8.\,27.\,1$$

is typical of acid-base reactions. The equilibrium condition is

$$\frac{m_B m_{A'}}{m_A m_{B'}} \frac{\gamma_B \gamma_{A'}}{\gamma_A \gamma_{B'}} = K \qquad 8.\,27.\,2$$

where K depends on the solvent and the temperature, but not on the composition of the solution. As a typical example we have, using Ac as an abbreviation for CH_3CO_2

$$NH_4^+ + Ac^- \rightarrow NH_3 + HAc \qquad 8.\,27.\,3$$

$$\frac{m_{NH_3} m_{HAc}}{m_{NH_4^+} m_{Ac^-}} \frac{\gamma_{NH_3} \gamma_{HAc}}{\gamma_{NH_4^+} \gamma_{Ac^-}} = K \qquad 8.\,27.\,4$$

Since water is both a base and an acid it can react with either an acid or a base dissolved in it. As examples of acids reacting with water, we mention

$$HAc + H_2O \rightarrow Ac^- + H_3O^+ \qquad 8.\,27.\,5$$

$$NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+ \qquad 8.\,27.\,6$$

$$H_2PO_4^- + H_2O \rightarrow HPO_4^{2-} + H_3O^+ \qquad 8.\,27.\,7$$
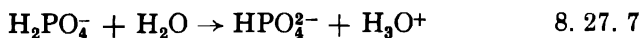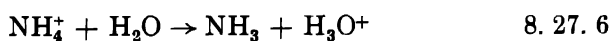
and as examples of bases reacting with water

$$H_2O + Ac^- \rightarrow OH^- + HAc \qquad 8.\,27.\,8$$

$$H_2O + NH_3 \rightarrow OH^- + NH_4^+ \qquad 8.\,27.\,9$$

$$H_2O + H_2PO_4^- \rightarrow OH^- + H_3PO_4 \qquad 8.\,27.\,10$$
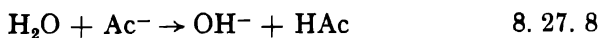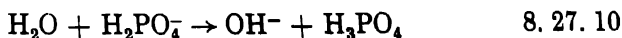
We note that according to the definition of *hydrolysis* given in the preceding section, reactions (5) to (10) are all examples of *hydrolysis*. On the other hand reaction (3) does not involve the solvent H_2O and is therefore not a *hydrolysis*.

The reactions (5), (6), (7) are all examples of the general type

$$A + H_2O \rightarrow B + H_3O^+ \qquad 8.\,27.\,11$$
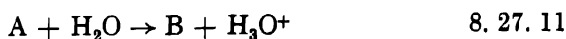
of which the equilibrium condition in dilute solution becomes

$$\frac{m_B \, m_{H_3O^+}}{m_A} \frac{\gamma_B \, \gamma_{H_3O^+}}{\gamma_A} = K_A \qquad 8.\,27.\,12$$

where K_A is called the *acidity constant* of A in water at the given temperature. K_A is a measure of the strength of the acid A relative to water. The reciprocal of K_A may likewise be regarded as a measure of the strength of the conjugate base B. For example the acidity constants K_{HAc} of HAc and $K_{NH_4^+}$ of NH_4^+ have the values at 25 °C

$$K_{HAc} = 1.75 \times 10^{-5} \text{ mole kg}^{-1} \qquad 8.\,27.\,13$$

$$K_{NH_4^+} = 6.1 \times 10^{-10} \text{ mole kg}^{-1} \qquad 8.\,27.\,14$$

Two molecules of H_2O can react together, the one acting as an acid, the other as a base, thus:

$$H_2O + H_2O \rightarrow OH^- + H_3O^+$$
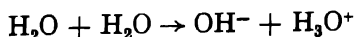
The equilibrium is determined by

$$m_{H_3O^+} \, m_{OH^-} \, \gamma_{H_3O^+} \, \gamma_{OH^-} = K_w \qquad 8.\,27.\,15$$

where K_w is called the *ionization product* of water. Its values at various temperatures are as follows:

$$0 \text{ °C} \quad K_w = 0.115 \times 10^{-14} \text{ mole}^2 \text{ kg}^{-2} \qquad 8.\,27.\,16$$

$$20 \text{ °C} \quad K_w = 0.68 \;\; \times 10^{-14} \text{ mole}^2 \text{ kg}^{-2} \qquad 8.\,27.\,17$$

$$25 \text{ °C} \quad K_w = 1.01 \;\; \times 10^{-14} \text{ mole}^2 \text{ kg}^{-2} \qquad 8.\,27.\,18$$

The equilibrium constants for reactions of the type

$$H_2O + B \rightarrow OH^- + A \qquad 8.\,27.\,19$$
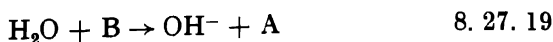
can always be expressed in terms of an acidity constant and the ionization constant of water. For example for reaction (8) we have

$$\frac{m_{OH^-} \, m_{HAc}}{m_{Ac^-}} \frac{\gamma_{OH^-} \, \gamma_{HAc}}{\gamma_{Ac^-}} = \frac{K_w}{K_{HAc}} \qquad 8.\,27.\,20$$

where K_{HAc} is the acidity constant K_A of HAc. Similarly for reaction(9) we have

$$\frac{m_{OH^-} \, m_{NH_4^+}}{m_{NH_3}} \frac{\gamma_{OH^-} \, \gamma_{NH_4^+}}{\gamma_{NH_3}} = \frac{K_w}{K_{NH_4^+}} \qquad 8.\,27.\,21$$

where $K_{NH_4^+}$ denotes the acidity constant of NH_4^+.

If we apply the definition (12) of an acidity constant to H_3O^+ we obtain

$$K_{H_3O^+} = \frac{m_{H_2O} \, m_{H_3O^+}}{m_{H_3O^+}} \frac{f_{H_2O} \, \gamma_{H_3O^+}}{\gamma_{H_3O^+}}$$

$$= m_{H_2O} \, f_{H_2O}$$

$$\simeq m_{H_2O} \simeq 55.5 \text{ mole kg}^{-1} \qquad 8.\,27.\,22$$

From (12) and (22) we see that no molecule or ion which is a much stronger acid than H_3O^+ can exist in appreciable quantity in water. For example HCl is a much stronger acid than H_3O^+. Consequently when dissolved in water it is almost completely changed to H_3O^+ and Cl^-. Similarly H_2SO_4 is a much stronger acid than H_3O^+ and is therefore almost completely changed to H_3O^+ and HSO_4^-. On the other hand $K_{HSO_4^-} = 1.0 \times 10^{-2}$ mole kg^{-1} so that HSO_4^- being a much weaker acid than H_3O^+ exists in appreciable amount in water.

Similarly no base much stronger than OH^- can exist in appreciable quantity in water, since it would be hydrolysed to its conjugate acid and OH^-. Examples of bases too strong to exist in water are O^{2-} and NH_2^- which are hydrolysed as follows

$$H_2O + O^{2-} \rightarrow OH^- + OH^- \qquad 8.\,27.\,23$$

$$H_2O + NH_2^- \rightarrow OH^- + NH_3 \qquad 8.\,27.\,24$$
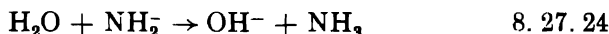
Examples of very strong bases, but not so strong that they cannot exist at all in water are S^{2-} and CN^-.

When a strongly alkaline substance such as NaOH is dissolved in water, the base present in the solution is OH^-. Often NaOH is itself referred to loosely as a base.

Similar relations hold in other solvents which can react as both base and acid. Reactions of an ion or molecule with the solvent are called *solvolysis*.

§ 8. 28 WEAK ELECTROLYTES

An electrically neutral molecule, not itself an electrolyte, which by hydrolysis or other reaction is partly changed into ions is sometimes called a *weak electrolyte*. In particular an electrically neutral acid such as HAc which is partly hydrolysed according to

$$HAc + H_2O \rightarrow Ac^- + H_3O^+ \qquad \text{8. 28. 1}$$

and an electrically neutral base such as NH_3 which is partly hydrolysed according to

$$H_2O + NH_3 \rightarrow OH^- + NH_4^+ \qquad \text{8. 28. 2}$$
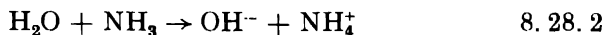
are according to this definition *weak electrolytes*. For these substances the names *electrically neutral acids* and *electrically neutral bases* are sufficient and more informative.

§ 8. 29 SURFACE PHASES

The formulae previously derived for surface phases apply just as well to solutions of electrolytes as to solutions of non-electrolytes. In particular for variations of composition at constant temperature formula (6. 28. 1) becomes

$$- d\gamma = \Sigma_i \left(\Gamma_i - r_i \Gamma_1 \right) D\mu_i \qquad \text{8. 29. 1}$$

where the summation Σ_i extends over all ions and other solute species. Expressed in terms of absolute activities (1) becomes

$$- d\gamma = RT\Sigma_i \left(\Gamma_i - r_i \Gamma_1 \right) D \ln \lambda_i \qquad \text{8. 29. 2}$$

Even if the solution is extremely dilute the term $r_i \Gamma_1$ must not be omitted for although $r_i \ll 1$ at the same time $|\Gamma_1| \gg |\Gamma_i|$.

The above relations, and in fact all the relations, for the surface of an electrolyte solution are formally analogous to those for the surface of a non-electrolyte solution. There is however a significant difference requiring careful treatment, namely counting the number of independent components. Let us consider some typical examples beginning with the simplest.

A solution of hydrochloric acid in water contains the species H_2O,

H_3O^+ and Cl^-. We omit OH^-, not so much because it is present in negligible amount as because it is in any case not an independent component, since

$$OH^- = 2H_2O - H_3O^- \qquad 8.\ 29.\ 3$$

Of the three species H_2O, H_3O^+ and Cl^- the condition for electrical neutrality imposes the restrictions

$$m_{H_3O^+} = m_{Cl^-} \qquad 8.\ 29.\ 4$$

$$\Gamma_{H_3O^+} = \Gamma_{Cl^-} \qquad 8.\ 29.\ 5$$

so that there are only two independent components. We may take these to be H_2O on the one hand and $(H_3O^+ + Cl^-)$ on the other. More simply we may choose as independent components H_2O and HCl.

Similarly a solution of sodium hydroxide in water contains the species H_2O, OH^- and Na^+. We omit H_3O^+ not so much because it is present in negligible amount as because it is in any case not an independent component owing to (3). The condition for electrical neutrality imposes the restrictions

$$m_{OH^-} = m_{Na^+} \qquad 8.\ 29.\ 6$$

$$\Gamma_{OH^-} = \Gamma_{Na^+} \qquad 8.\ 29.\ 7$$

so that there are only two independent components which we may take to be H_2O and NaOH. Thus for the surface tension of the solution of NaOH we have

$$- d\gamma = RT \left(\Gamma_{Na^+} - r_{Na^+}\Gamma_{H_2O} \right) D \ln \lambda_{Na^+}$$

$$+ RT \left(\Gamma_{OH^-} - r_{OH^-}\Gamma_{H_2O} \right) D \ln \lambda_{OH}$$

$$= 2RT \left(\Gamma_{NaOH} - r_{NaOH}\Gamma_{H_2O} \right) D \ln m_{NaOH}\, \gamma_{Na,OH} \qquad 8.\ 29.\ 8$$

where m_{NaOH} and Γ_{NaOH} are defined by

$$m_{Na^+} = m_{OH^-} = m_{NaOH} \qquad 8.\ 29.\ 9$$

$$\Gamma_{Na^+} = \Gamma_{OH^-} = \Gamma_{NaOH} \qquad 8.\ 29.\ 10$$

respectively.

The reader should have no difficulty in distinguishing between γ without any subscript denoting surface tension and $\gamma_{Na,OH}$ denoting the mean activity coefficient of NaOH.

Let us now consider a solution made by dissolving both hydrogen chloride and sodium hydroxide in water. Of the five species H_2O, H_3O^+, OH^-, Na^+ and Cl^- in the system only three are independent. For the equilibrium

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^- \qquad 8.\ 29.\ 11$$
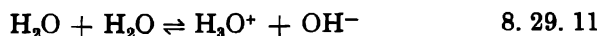
imposes the restriction

$$m_{H_3O^+}\, m_{OH^-}\, \gamma_{H_3O^+}\, \gamma_{OH^-} = K_w \qquad 8.\ 29.\ 12$$

and the condition for electrical neutrality imposes the restrictions

$$m_{Na^+} + m_{H_3O^+} = m_{Cl^-} + m_{OH^-} \qquad 8.\ 29.\ 13$$

$$\Gamma_{Na^+} + \Gamma_{H_3O^+} = \Gamma_{Cl^-} + \Gamma_{OH^-} \qquad 8.\ 29.\ 14$$

If the hydrogen chloride is in excess, it is natural to choose as the three independent components H_2O, NaCl and HCl. In this case m_{OH^-} is negligible compared with all the other terms in (13). If on the contrary the sodium hydroxide is in excess, it is natural to choose as the three independent components H_2O, NaCl and NaOH. In this case $m_{H_3O^+}$ is negligible compared with the other terms in (13). These remarks apply equally to the bulk of the solution and to the surface layer.

Suppose now we stipulate that precisely equivalent amounts of hydrogen chloride and sodium hydroxide are contained in the solution. Then the relation (13) is replaced by the two relations

$$m_{Na^+} = m_{Cl^-} \qquad 8.\ 29.\ 15$$

$$m_{H_3O^+} = m_{OH^-} \qquad 8.\ 29.\ 16$$

so that the solution contains only two independent components, which we naturally take to be H_2O and NaCl. But the restriction (15) which reduces by one the number of independent components in the bulk of the solution, does not imply any analogous restriction on the Γ's. In other words the surface layer can contain as well as H_2O and NaCl either an excess of HCl or an excess of NaOH. Thus the number of components necessary to describe the composition of the surface phase is still three, not two.

We shall now analyse this problem, beginning with unspecified quantities of NaCl and NaOH dissolved in water, introducing the restriction that the quantity of NaOH is zero only at a later stage. There are four ionic species Na^+, Cl^-, H_3O^+ and OH^- in the solvent

H_2O. These are not independent, but are subject to the conditions for electrical neutrality

$$m_{Na^+} + m_{H_3O^+} = m_{Cl^-} + m_{OH^-} \qquad 8.\ 29.\ 17$$

$$\Gamma_{Na^+} + \Gamma_{H_3O^+} = \Gamma_{Cl^-} + \Gamma_{OH^-} \qquad 8.\ 29.\ 18$$

and to the condition for ionization equilibrium of the solvent water

$$\lambda_{H_3O^+}\,\lambda_{OH^-} = \lambda_{H_2O}^2 = \text{const.} \qquad 8.\ 29.\ 19$$

For variations of the surface tension with composition at constant temperature we have the general relation of the form (2)

$$-\frac{d\gamma}{RT} = (\Gamma_{Na^+} - r_{Na^+}\Gamma_{H_2O})\ D \ln \lambda_{Na^+}$$
$$+ (\Gamma_{Cl^-} - r_{Cl^-}\Gamma_{H_2O})\ D \ln \lambda_{Cl^-}$$
$$+ (\Gamma_{H_3O^+} - r_{H_3O^+}\Gamma_{H_2O})\ D \ln \lambda_{H_3O^+}$$
$$+ (\Gamma_{OH^-} - r_{OH^-}\Gamma_{H_2O})\ D \ln \lambda_{OH^-} \qquad 8.\ 29.\ 20$$

Using (17), (18) and (19) we can replace (20) by

$$-\frac{d\gamma}{RT} = (\Gamma_{Cl^-} - r_{Cl^-}\Gamma_{H_2O})\ D \ln \lambda_{Na^+}\,\lambda_{Cl^-}$$
$$+ ([\Gamma_{Na^+} - \Gamma_{Cl^-}] - [r_{Na^+} - r_{Cl^-}]\,\Gamma_{H_2O})\ D \ln \lambda_{Na^+}\,\lambda_{OH^-}$$
$$= (\Gamma_{Cl^-} - r_{Cl^-}\Gamma_{H_2O})\ D \ln m_{Na^+}\,m_{Cl^-}\,\gamma_{Na,Cl}^2$$
$$+ ([\Gamma_{Na^+} - \Gamma_{Cl^-}] - [r_{Na^+} - r_{Cl^-}]\,\Gamma_{H_2O})\ D \ln m_{Na^+}m_{OH^-}\,\gamma_{Na,OH}^2$$

$$8.\ 29.\ 21$$

Thus by studying the dependence of the surface tension γ on the composition by variations of the molalities of NaCl and of NaOH, provided the activity coefficients are known, we can determine the separate values of

$$\Gamma_{Cl^-} - r_{Cl^-}\,\Gamma_{H_2O} \qquad 8.\ 29.\ 22$$

and of

$$[\Gamma_{Na^+} - \Gamma_{Cl^-}] - [r_{Na^+} - r_{Cl^-}]\,\Gamma_{H_2O} \qquad 8.\ 29.\ 23$$

The expression (22) is a measure of the adsorption of NaCl relative to H_2O, while the expression (23) is a measure of the adsorption of

NaOH relative to H_2O. In particular as the molality of NaOH is made to tend to zero, so the quantity (23) tends to

$$\Gamma_{Na^+} - \Gamma_{Cl^-} \qquad \qquad 8.\ 29.\ 24$$

The value of (24) then becomes the surface concentration of NaOH in a solution which in the bulk contains only NaCl and H_2O.

To recapitulate, by varying the molalities of both NaCl and NaOH and measuring surface tension we can determine separately the coefficients of the two terms on the right of (21) namely the quantities (22) and (23), of which the latter reduces to (24) in a solution containing no excess NaOH. By measuring the surface tension of solutions containing varying amounts of NaCl only without any NaOH it is not possible to separate the two terms on the right of (21) and consequently the quantity (22) can not be determined in this way.

ELECTROCHEMICAL SYSTEMS

§ 9. 01 ELECTRICALLY CHARGED PHASES

In the previous chapter we saw how a solution containing ions can be treated by means of the same formulae as one containing only electrically neutral molecules. In particular the formulae

$$dF = - SdT - PdV + \Sigma_i \mu_i \, dn_i \qquad 9.\,01.\,1$$

$$dG = - SdT + VdP + \Sigma_i \mu_i \, dn_i \qquad 9.\,01.\,2$$

from which follows

$$\mu_i = \left(\frac{\partial F}{\partial n_i}\right)_{T,V,n_j} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} \qquad 9.\,01.\,3$$

are applicable. The only significant difference in our treatment of ions was the imposition of the condition for electrical neutrality

$$\Sigma_i \, n_i z_i = 0 \qquad 9.\,01.\,4$$

where z_i is the charge number of the ionic species i. We shall now consider what happens if we try to relax the condition (4).

To obtain a clear picture of what happens it is useful to begin with some simple numerical calculations. The charge e on a proton is given by

$$e = 1.6020 \times 10^{-19} \, C \qquad 9.\,01.\,5$$

Consequently the electric charge, associated with one mole of an ionic species having a charge number 1, called the *faraday* and denoted by F is given by

$$F = Le = 0.96497 \times 10^5 \, C \, mole^{-1} \qquad 9.\,01.\,6$$

Let us now consider a single phase surrounded by empty space and thus electrically insulated. Let us further imagine that this phase, instead of satisfying the condition of electrical neutrality (4), contains an excess of 10^{-10} moles of an ionic species with charge number $+ 1$. Then most, if not all, the excess electrical charge will accumulate at the surface of the phase. For simplicity let us suppose that the phase is

spherical with a radius one centimetre. The electrical potential ψ of a charged sphere of radius r in vacuo is determined by

$$\psi = \frac{Q}{\varepsilon_0 r} \qquad 9.01.7$$

where Q is the charge on the sphere and ε_0 is the permittivity of free space. Substituting the values

$$Q = 10^{-10} \text{ mole F} = 0.96 \times 10^{-5} \text{ C}$$
$$\varepsilon_0 = 1.11 \times 10^{-10} \text{ C V}^{-1} \text{ m}^{-1}$$
$$r = 10^{-2} \text{ m} \qquad 9.01.8$$

into (7), we obtain

$$\psi = \frac{0.96 \times 10^{-5}}{1.11 \times 10^{-10} \times 10^{-2}} \text{ V} = 0.86 \times 10^7 \text{ V} \qquad 9.01.9$$

From this example we have reached the striking conclusion that a departure from the condition of electrical neutrality corresponding to a quantity of ions far too small to be detected chemically corresponds to an electrostatic potential which could be encountered only in specialized high voltage laboratories. Any other numerical example would lead to the same conclusion.

§ 9.02 PHASES OF IDENTICAL COMPOSITION

The above general result leads to the use of the following terminology. We speak of two phases having the *same chemical content*, but *different electrical potentials*. Actually two such phases differ in chemical content but the difference is too small to be detectable by chemical means, or any other means, except electrical. For example suppose we mention two spheres of copper each containing precisely one gram, differing in electrical potential by 200 volts. If this electrical potential difference is ascribed to an excess of copper ions Cu^{2+} with an electrovalency $+2$, then the amount of this excess is about 3.5×10^{-16} moles or 2×10^{-14} grams. This excess is so small as to be entirely negligible except in its electrical effect. Consequently it is of no importance or interest whether the electrical charge is in fact due to an excess of Cu^{2+} ions or to an equivalent deficiency of electrons or even to some extraneous kind of ion such as H_3O^+, present as an impurity.

Similar considerations apply to a pair of phases of different size but of the same chemical composition.

§ 9. 03 ELECTROCHEMICAL POTENTIALS

Having agreed as to what we mean when we speak of two phases having the same chemical composition but different electrical potentials, we see that the μ_i's occurring in the formulae mentioned in § 9. 01 have values depending on the electrical state of the phase as well as on its chemical composition. To stress this fact we call the μ_i of an ionic species its *electrochemical potential.* *

The difference of the electrochemical potential μ_i between two phases of *identical chemical composition* will clearly be proportional to the electrical charge $z_i F$ associated with a mole of the species in question but independent of all its other individual characteristics. Hence for any two phases α and β of identical chemical composition and any ionic species i we may write

$$\mu_i^\beta - \mu_i^\alpha = z_i F \left(\psi^\beta - \psi^\alpha \right) \qquad 9. 03. 1$$

where $\psi^\beta - \psi^\alpha$ is the *electrical potential difference* between the two phases. Formula (1) may be regarded as the thermodynamic definition of the electrical potential difference between two phases of *identical chemical composition*. The equilibrium condition for a given ionic species between two phases of identical composition is that the two phases should be at the same electrical potential. In fact the laws of mathematical electrostatics are applicable to any ionic species, in particular to electrons, only in so far as differences in chemical composition between several phases are excluded or ignored.

For the distribution of the ionic species i between two phases α, β of different chemical composition the equilibrium condition is equality of the electrochemical potential μ_i, that is to say

$$\mu_i^\alpha = \mu_i^\beta \qquad 9. 03. 2$$

Any splitting of $\mu_i^\beta - \mu_i^\alpha$ into a chemical part and an electrical part is in general arbitrary and without physical significance.

As long ago as 1899 Gibbs † wrote: "Again, the consideration of the electrical potential in the electrolyte, and especially the consideration of the difference of potential in electrolyte and electrode, involve the consideration of quantities of which we have no apparent means of physical measurement, while the difference of potential in pieces of metal of the same kind attached to the electrodes is exactly one of the

* Guggenheim, *J. Phys. Chem.* 1929 **33** 842.

† Gibbs, *Collected Works* vol. 1. p. 429.

things which we can and do measure." This principle was however ignored or forgotten until rediscovered and reformulated thirty years later as follows: * "The electric potential difference between two points in different media can never be measured and has not yet been defined in terms of physical realities. It is therefore a conception which has no physical significance." The electrostatic potential difference between two points is admittedly defined in *electrostatics*, the mathematical theory of an imaginary fluid *electricity*, whose equilibrium or motion is determined entirely by the electric field. *Electricity* of this kind does not exist. Only electrons and ions have physical existence and these differ fundamentally from the hypothetical fluid *electricity* in that their equilibrium is *thermodynamic* not *electrostatic*.

Although the above considerations seem almost obvious to anyone who has thought about the matter, there has in the past been considerable confusion due to misleading terminology. It therefore seems worth while considering in more detail some simple examples. Consider a potentiometer wire made of say copper and in particular two sections of the wire a' and a'' between which the electrical potential difference $\psi'' - \psi'$ is say 2V. Since a' and a'' are both in copper, there is no ambiguity in the meaning of $\psi'' - \psi'$. If two pieces of copper wire are attached to a' and a'', then the electrical potential difference between these two is also $\psi'' - \psi' = 2V$. If instead of copper wire we attach two pieces of silver wire β' and β'' to a' and a'' respectively, then the difference of electrical potential between β' and β'' is likewise 2V. The electrical potential difference between a piece of copper and a piece of silver is however not defined. The silver wire β' and the copper wire a' are in equilibrium with respect to electrons, so that

$$\mu_{\text{el}^-}^{a'} = \mu_{\text{el}^-}^{\beta'} \qquad 9.\,03.\,3$$

where the subscript $_{\text{el}^-}$ denotes electrons. Likewise

$$\mu_{\text{el}^-}^{a''} = \mu_{\text{el}^-}^{\beta''} \qquad 9.\,03.\,4$$

Thus the situation is completely described by (3) or (4) together with

$$\mu_{\text{el}^-}^{a''} - \mu_{\text{el}^-}^{a'} = \mu_{\text{el}^-}^{\beta''} - \mu_{\text{el}^-}^{\beta'} = -\,F\,(\psi'' - \psi') \qquad 9.\,03.\,5$$

Suppose further that the two pieces of silver wire β', β'' be dipped respectively into two solutions γ', γ'' both having the same composition and both containing a silver salt. Then between each piece of silver wire

* Guggenheim, *J. Phys. Chem.* 1929 **33** 842.

and the solution with which it is in contact there will be equilibrium with respect to silver ions Ag^+. Hence

$$\mu_{Ag^+}^{\gamma'} = \mu_{Ag^+}^{\beta'} \qquad \qquad 9.\,03.\,6$$

$$\mu_{Ag^+}^{\gamma''} = \mu_{Ag^+}^{\beta''} \qquad \qquad 9.\,03.\,7$$

At the same time

$$\mu_{Ag^+}^{\gamma''} - \mu_{Ag^+}^{\gamma'} = \mu_{Ag^+}^{\beta''} - \mu_{Ag^+}^{\beta'} = F\,(\psi'' - \psi') = F \times 2V \qquad 9.\,03.\,8$$

If the two solutions γ', γ'' are contained in insulating vessels and the silver wires are removed without otherwise touching or disturbing the two solutions then the relations (8) remain valid until one solution is touched by some other electrically charged or electrically conducting body. From this it is clear that the value of μ_{Ag^+} in a solution of a silver salt depends not only on the composition of the solution but also on its, usually accidentally determined, electrical state. If the solutions also contain nitrate ions NO_3^- then, since both solutions have the same composition,

$$\mu_{NO_3}^{\gamma''} - \mu_{NO_3}^{\gamma'} = - F\,(\psi'' - \psi') \qquad \qquad 9.\,03.\,9$$

Adding (8) and (9), we obtain

$$\mu_{Ag^+}^{\gamma'} + \mu_{NO_3^-}^{\gamma'} = \mu_{Ag^+}^{\gamma''} + \mu_{NO_3^-}^{\gamma''} \qquad \qquad 9.\,03.\,10$$

the electrical terms cancelling. We accordingly speak of the *chemical potential* of a salt, for example $\mu_{Ag,\,NO_3} = \mu_{Ag^+} + \mu_{NO_3^-}$, but of the *electrochemical potentials* of ions, for example μ_{Ag^+} and μ_{NO_3}.

§ 9. 04 ABSOLUTE ACTIVITIES OF IONS

Since the absolute activity λ_i is related to μ_i by

$$\mu_i = RT \ln \lambda_i$$

it is clear that the absolute activity of an ionic species contains a factor depending on the, usually accidentally determined, electrical state of the system. The same applies to the activity coefficient of an ionic species. As already emphasized in the previous chapter all such indeterminacy disappears in formulae relating to electrically neutral combinations of ions, in particular to salts.

§ 9. 05 DILUTE SOLUTIONS IN COMMON SOLVENT

According to (8. 09. 1) the absolute activity λ_i of an ionic species i is related to its molality m_i and its activity coefficient γ_i by

$$\lambda_i = \lambda_i^{\ominus}\, m_i\, \gamma_i \qquad\qquad 9.\ 05.\ 1$$

where $\lambda_i^{\ominus}$ depends on the solvent and temperature and moreover contains a partly undetermined factor, which however cancels in all applications to processes not involving a net transfer of electrical charge. Correspondingly the electrochemical potential μ_i has the form

$$\mu_i = RT \ln \lambda_i^{\ominus} + RT \ln m_i + RT \ln \gamma_i \qquad\qquad 9.\ 05.\ 2$$

and includes an undetermined additive term which cancels in all applications to processes not involving a net transfer of electrical charge. We shall investigate this term in greater detail.

Let us formally write

$$\mu_i = z_i F \psi + RT \ln l_i^{\ominus} + RT \ln m_i + RT \ln \gamma_i \qquad\qquad 9.\ 05.\ 3$$

where $l_i^{\ominus}$ is independent of the electrical state of the phase and ψ is the electrical potential of the phase. Let us now apply (3) to two phases denoted by a single and a double dash respectively and then subtract. We obtain

$$\mu_i'' - \mu_i' = z_i F\,(\psi'' - \psi') + RT \ln \frac{l_i^{\ominus''}}{l_i^{\ominus'}} + RT \ln \frac{m_i''}{m_i'}$$
$$+ RT \ln \frac{\gamma_i''}{\gamma_i'} \qquad\qquad 9.\ 05.\ 4$$

We now reexamine the condition for the term containing $(\psi'' - \psi')$ to be physically defined.

The easiest case is when the two phases have the same chemical composition so that

$$l_i^{\ominus''} = l_i^{\ominus'} \qquad\qquad 9.\ 05.\ 5$$

$$m_i'' = m_i' \qquad\qquad 9.\ 05.\ 6$$

$$\gamma_i'' = \gamma_i' \qquad\qquad 9.\ 05.\ 7$$

Formula (4) then reduces to

$$\mu_i'' - \mu_i' = z_i F\,(\psi'' - \psi') \qquad\qquad 9.\ 05.\ 8$$

Since $\mu_i'' - \mu_i'$ is always well defined, formula (8) in this special case defines $\psi'' - \psi'$.

We now consider the extreme opposite case of two solutions in different solvents or two different pure phases. This is the case in which there is no means of distinguishing in (4) between the term containing $\psi'' - \psi'$ and the term containing $l_i^{\ominus''}/l_i^{\ominus'}$. The splitting into these two terms has in this case no physical significance. These remarks merely repeat and confirm what has already been stated in the preceding sections.

We have still to consider the intermediate case of two solutions of different composition in the same solvent, of course at the same temperature. We then have

$$l_i^{\ominus''} = l_i^{\ominus'} \qquad\qquad 9.\,05.\,9$$

so that (4) reduces to

$$\mu_i'' - \mu_i' = z_i \mathrm{F}\,(\psi'' - \psi') + RT \ln \frac{m_i''}{m_i'} + RT \ln \frac{\gamma_i''}{\gamma_i'} \qquad 9.\,05.\,10$$

Since $\mu_i'' - \mu_i'$ is well defined and m_i'', m_i' are measurable, the question whether $\psi'' - \psi'$ is determinate depends on our knowledge of γ_i''/γ_i'. If both the solutions are so dilute that we can evaluate γ_i by an explicit formula such as (8.19.2), then we may consider that (10) defines $\psi'' - \psi'$. If on the other hand either solution is so concentrated that our knowledge of the value of γ_i is incomplete, then the value of $\psi'' - \psi'$ becomes correspondingly indefinite.

§ 9. 06 VOLTA POTENTIALS

It is outside the province of this book to consider thermionic phenomena. In case however any reader may be puzzled by the fact that the so-called *Volta potential difference* or *contact potential difference* between two metals can be determined, it seems worth while stressing that the only measurable potential difference of this kind is that between two regions in free space immediately *outside* the two metals respectively.

§ 9. 07 MEMBRANE EQUILIBRIUM (NON-OSMOTIC)

Suppose two solutions α and β at the same temperature and pressure in the same solvent be separated by a membrane permeable to some ions, but not to others, nor to the solvent. We call this a *non-osmotic membrane equilibrium*. Then for every permeant ion we have the equilibrium condition

$$\mu_i^\alpha = \mu^\beta \qquad\qquad 9.\,07.\,1$$

If for example one of the permeant ions is the Ag^+ ion, we have

$$\mu^a_{Ag^+} = \mu^\beta_{Ag^+} \qquad\qquad 9.\,07.\,2$$

If then we place in each of the two solutions a piece of silver wire since each piece of wire is in equilibrium, with respect to Ag^+, with the solution in which it dips, the equality of μ_{Ag^+} also holds between the two pieces of silver wire. Hence the two pieces of silver wire have equal electrical potentials, as could be verified by connecting them to a voltmeter or electrometer.

We have yet to consider what, if anything, can be said concerning the electrical potential difference between the two solutions. Since the solvent is the same in both solutions, we may in accordance with (9. 05. 10) replace (2) by

$$F\,(\psi^\beta - \psi^a) + RT \ln \frac{m^\beta_{Ag^+}}{m^a_{Ag^+}} + RT \ln \frac{\gamma^\beta_{Ag^+}}{\gamma^a_{Ag^+}} = 0 \qquad 9.\,07.\,3$$

Supposing that m_{Ag^+} has been measured in both solutions, the determination of $\psi^\beta - \psi^a$ reduces to that of the values of γ_{Ag^+} in the two solutions. If the solutions are so dilute that accurate or at least approximate, formulae for the activity coefficients γ are available then the electrical potential difference $\psi^\beta - \psi^a$ can be evaluated with greater or less accuracy as the case may be. If either solution is so concentrated that γ_{Ag^+} cannot be evaluated, then no more can $\psi^\beta - \psi^a$.

If there are several permeant ions, then the relations of the form (1) can be combined into relations corresponding to processes involving no net flow of electric charge. For example for a salt consisting of ν_+ cations R of charge number z_+ and ν_- anions X of charge number z_-, both permeant, the equilibrium condition is

$$\nu_+\,\mu^a_R + \nu_-\,\mu^a_X = \nu_+\,\mu^\beta_R + \nu_-\,\mu^\beta_X \qquad 9.\,07.\,4$$

which can be written in the equivalent form

$$(m^a_R)^{\nu_+}\,(m^a_X)^{\nu_-}\,(\gamma^a_{R,X})^{\nu_+ + \nu_-} = (m^\beta_R)^{\nu_+}\,(m^\beta_X)^{\nu_-}\,(\gamma^\beta_{R,X})^{\nu_+ + \nu_-} \quad 9.\,07.\,5$$

§ 9. 08 OSMOTIC MEMBRANE EQUILIBRIUM

In the preceding section we assumed that the membrane was impermeable to the solvent. The more usual case when the membrane is permeable to the solvent, called *osmotic membrane equilibrium*, is less simple. In this case equilibrium as regards the solvent between two

phases separated by the membrane, will generally require a pressure difference between the two phases, the *osmotic pressure difference*, and this pressure difference complicates the exact conditions of equilibrium for the solute ions. We shall consider only the case of one and the same solvent on both sides of the membrane.

The conditions for membrane equilibrium can be written in the general form

$$\mu_1^a = \mu_1^\beta \tag{9. 08. 1}$$

for the solvent and

$$\mu_i^a = \mu_i^\beta \tag{9. 08. 2}$$

for each permeant ionic species.

We have now to take account of how each μ depends on the pressure, but for the sake of brevity we shall neglect the compressibility of the solutions. We have then in accordance with (8. 06. 1)

$$\mu_1 (P) = \mu_1^0 (P) - RT\varphi \, \Sigma_i \, r_i$$
$$= \mu_1^{0\dagger} + PV_1 - RT\varphi \, \Sigma_i \, r_i \tag{9. 08. 3}$$

where $\mu_1^0 (P)$ is the value of μ_1 for the pure solvent at the pressure P, while $\mu_1^{0\dagger}$ is the value for the pure solvent in the limit of zero pressure.

Similarly for each ionic species i we replace (9. 05. 3) by

$$\mu_i = PV_i + z_i F\psi + RT \ln l_i^{\ominus\dagger} + RT \ln m_i \, \gamma_i \tag{9. 08. 4}$$

where $l_i^{\ominus\dagger}$ is independent of the pressure.

Using (3) in (1) we obtain for the equilibrium value of the pressure difference

$$P^\beta - P^a = \frac{RT}{V_1} (\varphi^\beta \, \Sigma_i \, r_i^\beta - \varphi^a \, \Sigma_i \, r_i^a) \tag{9. 08. 5}$$

Using (4) in (2) we obtain

$$RT \ln \frac{m_i^\beta \, \gamma_i^\beta}{m_i^a \, \gamma_i^a} + z_i F \, (\psi^\beta - \psi^a) = (P^a - P^\beta) \, V_i \tag{9. 08. 6}$$

and then substituting (5) into (6)

$$\ln \frac{m_i^\beta \, \gamma_i^\beta}{m_i^a \, \gamma_i^a} + \frac{z_i F}{RT} (\psi^\beta - \psi^a) = \frac{V_i}{V_1} (\varphi^a \, \Sigma_i \, r_i^a - \varphi^\beta \, \Sigma_i \, r_i^\beta) \tag{9. 08. 7}$$

Whether formula (7) by itself has any physical significance depends, as explained in § 9. 05, on whether values of γ_i can be computed. If they

can, then from formula (7) the value of $\psi^\beta - \psi^\alpha$ can be computed, since all the other quantities occurring in (7) are measurable. In any case the term containing $\psi^\beta - \psi^\alpha$ can be eliminated by applying (7) to several ionic species together forming an electrically neutral combination. Thus for the equilibrium distribution of a permeant electrolyte consisting of ν_+ cations R and ν_- anions X we obtain

$$\frac{(m_R^\beta)^{\nu_+} (m_X^\beta)^{\nu_-} (\gamma_{R,X}^\beta)^{\nu_+ + \nu_-}}{(m_R^\alpha)^{\nu_+} (m_X^\alpha)^{\nu_-} (\gamma_{R,X}^\alpha)^{\nu_+ + \nu_-}}$$

$$= \exp\left\{\frac{\nu_+ V_R + \nu_- V_X}{V_1}\left(\varphi^\alpha \Sigma_i r_i^\alpha - \varphi^\beta \Sigma_i r_i^\beta\right)\right\} \qquad 9.\,08.\,8$$

At high dilutions when all $r_i \ll 1$ the quantity within the { } on the right side of (8) may be so small that it can be neglected. Under such conditions (8) reduces to

$$(m_R^\beta)^{\nu_+} (m_X^\beta)^{\nu_-} (\gamma_{R,X}^\beta)^{\nu_+ + \nu_-} = (m_R^\alpha)^{\nu_+} (m_X^\alpha)^{\nu_-} (\gamma_{R,X}^\alpha)^{\nu_+ + \nu_-} \qquad 9.\,08.\,9$$

of the same form as (9. 07. 5) for a non-osmotic membrane equilibrium.

The thermodynamic methods of Gibbs were first applied to osmotic membrane equilibria by Donnan. Such an equilibrium is accordingly called *Donnan's membrane equilibrium*.

§ 9. 09 CONTACT EQUILIBRIUM

The most important and simplest example of non-osmotic equilibrium is that of two phases with one common ion, the surface of separation being in effect a membrane permeable to the common ion but impermeable to all others. This may be called *contact equilibrium*.

We have already met several examples of contact equilibrium. For example, for two metals say Cu and Ag in contact there is equilibrium between the metals as regards electrons, but not as regards the positive ions Cu^{2+} or Ag^+. This equilibrium is expressed by

$$\mu_{el^-}^{Cu} = \mu_{el^-}^{Ag} \qquad 9.\,09.\,1$$

the subscript $_{el^-}$ denoting electrons and the superscripts denoting the two phases.

Likewise for a piece of metal M of say Cu dipping into a solution S containing ions of the metal, in this case Cu^{2+}, the contact equilibrium is completely described by

$$\mu_{Cu^{2+}}^{M} = \mu_{Cu^{2+}}^{S} \qquad 9.\,09.\,2$$

the metal and solution being in mutual equilibrium as regards the metallic ions only.

In neither of these cases is any contact electrical potential difference thermodynamically definable.

§ 9. 10 EXAMPLES OF ELECTROCHEMICAL CELL

We shall now introduce the subject of electrochemical cells by the detailed study of a simple example in terms of the electrochemical potentials. At a later stage we shall proceed to derive more general formulae applicable to all electrochemical cells.

We describe a cell symbolically by writing down in order a number of phases separated by vertical lines, each phase being in contact with the phases written down immediately to its left and right. For example

$$\text{Cu} \quad \text{Zn} \quad \begin{array}{c} \text{Solution } I \\ \text{containing Zn}^{2+} \end{array} \quad \begin{array}{c} \text{Solution } II \\ \text{containing Ag}^+ \end{array} \quad \text{Ag} \quad \text{Cu} \qquad 9.\,10.\,1$$
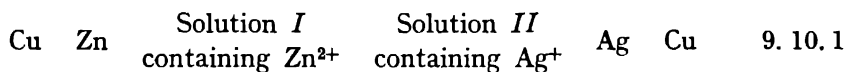
may be regarded as denoting a copper *terminal* attached to a zinc *electrode* dipping into a solution I containing zinc ions; this solution is in contact with another solution II containing silver ions in which there is dipping a silver electrode attached to another copper terminal. We shall use the following superscripts to denote the several phases:

'   the copper terminal on the left

$^{\text{Zn}}$ the zinc electrode

^{I} the solution on the left

^{II} the solution on the right

$^{\text{Ag}}$ the silver electrode

"   the copper terminal on the right

In the metal phases, since there is equilibrium between electrons, metallic ions and the metal atoms, we have

$$\mu'_{\text{Cu}^+} + 2\mu'_{\text{el}^-} = \mu''_{\text{Cu}^+} + 2\mu''_{\text{el}^-} = \mu^{\text{Cu}}_{\text{Cu}} \qquad 9.\,10.\,2$$

$$\mu^{\text{Zn}}_{\text{Zn}^+} + 2\mu^{\text{Zn}}_{\text{el}^-} = \mu^{\text{Zn}}_{\text{Zn}} \qquad 9.\,10.\,3$$

$$\mu^{\text{Ag}}_{\text{Ag}^+} + \mu^{\text{Ag}}_{\text{el}^-} = \mu^{\text{Ag}}_{\text{Ag}} \qquad 9.\,10.\,4$$

The contact equilibrium conditions are

$$\mu_{el^-} = \mu_{el^-}^{Zn} \qquad\qquad 9.\,10.\,5$$

$$\mu_{Zn^{2+}}^{Zn} = \mu_{Zn^{2+}}^{I} \qquad\qquad 9.\,10.\,6$$

$$\mu_{Ag^+}^{II} = \mu_{Ag^+}^{Ag} \qquad\qquad 9.\,10.\,7$$

$$\mu_{el^-}^{Ag} = \mu_{el^-}' \qquad\qquad 9.\,10.\,8$$

From (5) and (8) we deduce

$$\mu_{el^-}'' - \mu_{el^-}' = \mu_{el^-}^{Ag} - \mu_{el^-}^{Zn} \qquad\qquad 9.\,10.\,9$$

and so using (3) and (4)

$$\mu_{el^-}'' - \mu_{el^-}' = \mu_{Ag}^{Ag} - \tfrac{1}{2}\mu_{Zn}^{Zn} - \mu_{Ag^+}^{Ag} + \tfrac{1}{2}\mu_{Zn^{2+}}^{Zn} \qquad\qquad 9.\,10.\,10$$

and then using (6) and (7)

$$\mu_{el^-}'' - \mu_{el^-}' = \mu_{Ag}^{Ag} - \tfrac{1}{2}\mu_{Zn}^{Zn} - \mu_{Ag^+}^{II} + \tfrac{1}{2}\mu_{Zn^{2+}}^{I} \qquad\qquad 9.\,10.\,11$$

We may further write

$$\mu_{el^-}'' - \mu_{el^-}' = - F\,(\psi'' - \psi') \qquad\qquad 9.\,10.\,12$$

where $\psi'' - \psi'$ denotes the electrical potential difference between the two copper terminals. It is evident from relations (5) and (8) that the value of (12) would be the same if both copper terminals were replaced by any other metal provided both are of the same metal. Thus $\psi'' - \psi'$ is determined by the nature of the two electrodes and the two solutions. The electric potential difference $\psi'' - \psi'$ is called the *electromotive force* of the cell and is denoted by E. We accordingly replace (12) by

$$\mu_{el^-}'' - \mu_{el^-}' = - FE \qquad\qquad 9.\,10.\,13$$

Substituting (13) into (11) we then obtain

$$- FE = \mu_{Ag}^{Ag} - \tfrac{1}{2}\mu_{Zn}^{Zn} - \mu_{Ag^+}^{II} + \tfrac{1}{2}\mu_{Zn^{2+}}^{I} \qquad\qquad 9.\,10.\,14$$

We shall now assume that there is at least one anion, say NO_3^- present in both solutions I and II so that

$$\tfrac{1}{2}\mu_{Zn^{2+}}^{I} = \tfrac{1}{2}\mu_{Zn(NO_3)_2}^{I} - \mu_{NO_3^-}^{I} \qquad\qquad 9.\,10.\,15$$

$$\mu_{Ag^+}^{II} = \mu_{AgNO_3}^{II} - \mu_{NO_3^-}^{II} \qquad\qquad 9.\,10.\,16$$

Using (15) and (16) we can rewrite (14) as

$$FE = \{\tfrac{1}{2}\mu_{Zn}^{Zn} - \tfrac{1}{2}\mu_{Zn(NO_3)_2}^{I} + RT \ln m_{NO_3^-}^{I}\}$$

$$+ \left\{ \mu_{NO_3^-}^{I} - \mu_{NO_3^-}^{II} + RT \ln \frac{m_{NO_3^-}^{II}}{m_{NO_3^-}^{I}} \right\}$$

$$- \{\mu_{Ag}^{Ag} - \mu_{AgNO_3}^{II} + RT \ln m_{NO_3^-}^{II}\} \qquad\qquad 9.\,10.\,17$$

We have now a formula for E containing three terms in { } of which the first relates only to the Zn electrode and the solution around this electrode and the last relates only to the Ag electrode and the solution around this electrode. The middle term on the other hand is independent of the nature of the electrodes and relates to an anion present in both solutions. One might be inclined to call the first of these three terms the *electrode potential* of the Zn electrode, the second the *liquid-liquid junction potential* and the last the *electrode potential* of the silver. Such a procedure is harmless provided it is realized that

(a) this decomposition of E into three terms is affected by our arbitrary choice of the anion NO_3^- for use in our formulae;

b) other alternative decompositions of E into three terms can be obtained by the arbitrary choice of some other ion instead of NO_3^- in our formulae;

(c) any such decomposition of E is no more nor less fundamental than another;

(d) there is in general no means of decomposing E into three terms which is less arbitrary than the one described.

In view of some inevitable arbitrariness in the decomposition of the electromotive force of a cell into two *electrode potentials* and a *liquid-liquid junction potential*, we shall for the most part abandon any attempt at such a decomposition. We shall accordingly in the next section derive a general formula for the electromotive force of any cell by a more powerful method which makes no reference at all to the localization of separate terms in the electromotive force. Before proceeding to this general treatment, we shall however draw attention to a special case where the arbitrariness referred to above effectively disappears.

Reverting to formula (17), let us now consider the particular case where the molalities of Zn^{2+} and Ag^+ in the two electrode solutions are extremely small compared with the molalities of other ions in these solutions and the compositions of the two electrode solutions are apart from their content of Zn^{2+} and Ag^+ nearly identical. Under these particular conditions we may regard the two electrode solutions as effectively identical except with regard to the equilibrium between solution and electrode. We may accordingly drop the superscripts I and II so that (17) reduces to

$$FE = \{\tfrac{1}{2}\mu_{Zn}^{Zn} - \tfrac{1}{2}\mu_{Zn(NO_3)_2}\} - \{\mu_{Ag}^{Ag} - \mu_{AgNO_3}\} \qquad 9.\,10.\,18$$

where the μ's without superscripts refer to the solution. We may then regard the cell (1) under consideration as

$$\text{Cu} \quad \text{Zn} \quad \begin{matrix} \text{Solution containing} \\ \text{Zn}^{2+} \text{ and Ag}^+ \end{matrix} \quad \text{Ag} \mid \text{Cu} \qquad 9.\,10.\,19$$
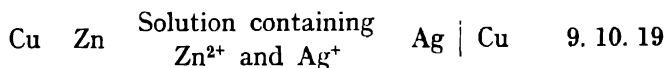
bearing in mind that in reality the Ag^+ must be kept away from the Zn electrode to avoid irreversible dissolution of Zn with plating out of Ag.

It is quite usual to describe certain cells in this manner as if containing only one solution, but in reality there must always be some real, though possibly small difference between the composition of the two electrode solutions. Consider for example the cell commonly described as

$$\text{Pt, H}_2 \quad \text{Aqueous solution of HCl} \mid \text{AgCl} \mid \text{Ag} \quad \text{Pt} \qquad 9.\,10.\,20$$

This description implies that an electrode consisting of platinum in contact with hydrogen and another electrode consisting of a mixture of AgCl and Ag are dipping into the same solution. In fact the platinum dips into a solution saturated with hydrogen, but containing no AgCl, while the silver is immersed in a solution saturated with AgCl but containing no hydrogen. If in fact any part of the solution contained both hydrogen and silver chloride, these might * react irreversibly to give silver and hydrogen chloride. Thus the cell is more accurately described by

$$\text{Pt, H}_2 \quad \begin{matrix} \text{Solution } I \\ \text{Aqueous solution} \\ \text{of HCl saturated} \\ \text{with H}_2 \end{matrix} \quad \begin{matrix} \text{Solution } II \\ \text{Aqueous solution} \\ \text{of HCl saturated} \\ \text{with AgCl} \end{matrix} \quad \text{AgCl} \quad \text{Ag} \quad \text{Pt}$$

$$9.\,10.\,21$$
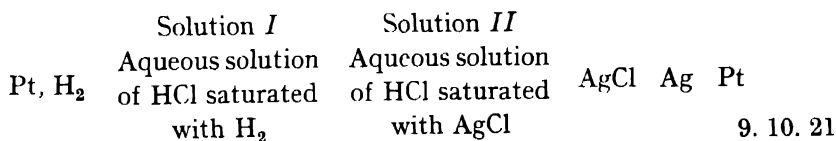
By an analysis of (21) similar to that applied to (1) it can be shown that the electromotive force is given accurately by

$$FE = \tfrac{1}{2}\mu_{\text{H}_2}^{\text{G}} - \mu_{\text{H}^+}^{I} + \mu_{\text{AgCl}}^{\text{AgCl}} - \mu_{\text{Ag}}^{\text{Ag}} - \mu_{\text{Cl}^-}^{II} \qquad 9.\,10.\,22$$

where the superscript $^{\text{G}}$ denotes the gas phase. Since however as far as the HCl is concerned we may regard the solutions I and II as essentially identical, we may drop these superscripts and (22) reduces to

$$FE = \tfrac{1}{2}\mu_{\text{H}_2}^{\text{G}} + \mu_{\text{AgCl}}^{\text{AgCl}} - \mu_{\text{Ag}}^{\text{Ag}} - \mu_{\text{HCl}} \qquad 9.\,10.\,23$$

where μ_{HCl} denotes the chemical potential of HCl in the solution.

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* Actually in the case of this cell the irreversible process will usually be too slow to affect the accuracy of the electromotive force measurements.

§ 9. 11 GENERAL TREATMENT OF ELECTROMOTIVE FORCE

We now proceed to a more general treatment applicable to any electro-chemical cell. We begin by describing the characteristics common to all such cells. In so doing it is convenient to assume that the system which we refer to as the *cell* is terminated at both ends by terminals of the same metal. The essential characteristic of the cell is that a chemical process involving ions can take place in it in such a manner that the process is necessarily accompanied by a transfer of electric charge from one terminal to the other without building up any charge in any of the intermediate phases of the cell. Moreover the charge which flows from the one terminal to the other is directly proportional to the change in the extent of the chemical reaction.

For example in the cell, already discussed in the previous section,

$$\text{Pt, } H_2 \mid \text{Aqueous solution of HCl} \mid \text{AgCl} \mid \text{Ag} \mid \text{Pt} \qquad 9. 11. 1$$

the chemical process accompanying the flow of one faraday from the left to the right is

$$\tfrac{1}{2}H_2\,(g) + AgCl\,(s) \rightarrow Ag\,(s) + HCl\,(aq) \qquad 9. 11. 2$$
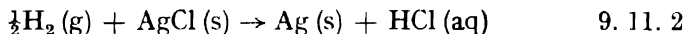
where (g) denotes gas, (s) denotes solid and (aq) denotes aqueous solution.

We now suppose the two terminals of the cell to be put into contact respectively with two points of a potentiometer bridge so placed that the electric potential of the right contact exceeds that of the left contact by an amount E'. Then in general an electric current will flow through the cell and between the two points of contact with the potentiometer bridge. If either of the points of contact is moved along the bridge the current will increase or decrease and it will change sign when E' has a certain value E. When E' is slightly less than E there will be a flow of current from left to right in the cell and from right to left in the potentiometer bridge; this flow of current will be accompanied by a well defined chemical change in the cell. When E' is slightly greater than E there will be a flow of current in the opposite direction and the accompanying chemical change in the cell will also be reversed. When E' is equal to E there will be no flow of current and no chemical change, but by a small shift in the point of contact between cell terminal and potentiometer bridge a small current can be made to flow in either direction. This is a typical and a particularly realistic example of a *reversible process*. The value E of E' at which the current changes sign is the *electromotive force* of the cell. We note that a

positive value of E means that the electrode on the right is positive.

We now stipulate that $E' = E$ so that the electromotive force of the cell is balanced against the potential difference in the potentiometer bridge and we consider the flow of one faraday from left to right in the cell, the temperature being maintained constant throughout and the pressure on every phase being kept constant. The pressures on different phases will usually, but not necessarily always, be all equal. Then since, as we have seen, this process is reversible and isothermal, it follows from (1. 41. 6) that the work w done on the cell is equal to the increase in free energy F, that is to say

$$w = \Delta F \qquad\qquad 9.\,11.\,3$$

In the present case w consists of two distinct parts, namely

(a) the work $- \Sigma_a P^a \, dV^a$ done by the pressures P^a acting on the several phases a,

(b) the electrical work $- FE$ done by the potentiometer on the cell in transferring one faraday through a potential difference E.

We may therefore replace (3) by

$$- FE = \Delta F + \Sigma_a P^a \, dV^a = \Delta G \qquad\qquad 9.\,11.\,4$$

It must be emphasized that the symbol Δ in both (3) and (4) denotes the increase of a function when the chemical change taking place is that associated with the flow in the cell of *one faraday from the left to the right*.

From (4) we see that the electrical work obtainable from a reversible isothermal process, at constant pressure on each phase, is equal to the decrease in the Gibbs function G.

Alternatively we could derive the relation

$$FE = A \qquad\qquad 9.\,11.\,5$$

where A denotes the *affinity* of the chemical process associated with the flow of one faraday from left to right. Formulae (4) and (5) are equivalent.

§ 9. 12 TEMPERATURE DEPENDENCE

By combining (9. 11. 4) with the Gibbs-Helmholtz relation (3. 06. 4) we obtain *

$$F\left(E - T\,\frac{\partial E}{\partial T}\right) = - \Delta H \qquad\qquad 9.\,12.\,1$$

* Although formula (3. 06. 4) is generally called the Gibbs-Helmholtz relation, it is in fact due to Gibbs, while its corollary (9. 12. 1) was derived by Helmholtz.

By subtracting (1) from (9. 11. 4), or by a more direct method, we obtain

$$F \frac{\partial E}{\partial T} = \Delta S \qquad\qquad 9.\ 12.\ 2$$

In both (1) and (2) the symbol Δ denotes increase when the chemical change takes place which accompanies the flow of one faraday from left to right in the cell.

It is perhaps worth while drawing attention to the physical meaning of ΔH and ΔS. If the cell is kept in a thermostat and balanced against a potentiometer so that any flow of current is reversible, then when one faraday flows from left to right in the cell

(a)   the work done on the cell by the potentiometer is $-FE$
(b)   the work done on the cell by external pressures is $-\Sigma_a P^a \Delta V^a$
(c)   the heat absorbed is $T\Delta S = FT\ (\partial E/\partial T)$
(d)   the increase in the energy of the cell is the sum of the above three terms namely $\Delta U = -FE - \Sigma_a P^a \Delta V^a + FT\ (\partial E/\partial T)$
(e)   the increase in the heat function is $\Delta H = \Delta U + \Sigma_a P^a \Delta V^a = -F\ \{E - T\ (\partial E/\partial T)\}$.

If, on the other hand, the cell is kept in a thermostat and short-circuited so that the chemical change takes place irreversibly without the performance of electrical work, then when the chemical change takes place to the same extent as before,

(a)   the electrical work done on the cell is zero
(b)   the work done on the cell by external pressures is $-\Sigma_a P^a \Delta V^a$
(c)   the heat absorbed is ΔH.

§ 9. 13 APPLICATION OF NERNST'S THEOREM

The measurement of electromotive force provides a method of determining ΔG for the accompanying chemical reaction; this can be combined with a value of ΔH, determined calorimetrically, so as to obtain the value of ΔS. Since however the magnitude of $T\Delta S$ is often small compared with that of ΔG and of ΔH, the relative error in ΔS determined in this way can be large. If on the other hand accurate measurements of electromotive force are made over a range of temperatures so as to give an accurate value of the temperature coefficient of the electromotive force, this provides directly the value of ΔS for the cell reaction. Values of ΔS thus obtained for any

chemical reaction between only solid phases may be used to test Nernst's heat theorem, provided heat capacity data down to low temperatures are available for each substance. The procedure is illustrated by the following example *.

In the cell

$$\text{Pt} \,\bigg|\, \text{Pb}^{\text{(Hg)}} \,\bigg|\, \begin{matrix} \text{Solution of Pb salt} \\ \text{saturated with PbI}_2 \end{matrix} \,\bigg|\, \text{PbI}_2 \,\bigg|\, \text{I} \,\bigg|\, \text{Pt} \qquad \text{9. 13. 1}$$
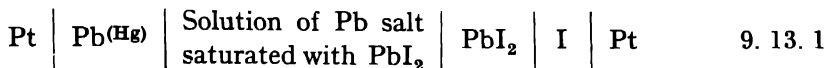
where the superscript $^{\text{(Hg)}}$ denotes that the lead is in the form of an amalgam, the chemical process when one faraday flows from left to right is

$$\tfrac{1}{2}\text{Pb}^{\text{(Hg)}} + \text{I} \rightarrow \tfrac{1}{2}\text{PbI}_2 \qquad \text{9. 13. 2}$$

For the cell at 25 °C it is found † that

$$E = 893.62 \, \text{mV} \qquad \text{9. 13. 3}$$

$$\frac{\partial E}{\partial T} = -0.042 \pm 0.005 \, \text{mV deg}^{-1} \qquad \text{9. 13. 4}$$

In the cell

$$\text{Pt} \,|\, \text{Pb}^{\text{(Hg)}} \,|\, \text{PbI}_2 \,|\, \text{Solution of KI} \,|\, \text{AgI} \,|\, \text{Ag} \,|\, \text{Pt} \qquad \text{9. 13. 5}$$

where $\text{Pb}^{\text{(Hg)}}$ denotes the same lead amalgam as in (1), the cell process accompanied by the flow of one faraday from left to right is

$$\tfrac{1}{2}\text{Pb}^{\text{(Hg)}} + \text{AgI} \rightarrow \tfrac{1}{2}\text{PbI}_2 + \text{Ag} \qquad \text{9. 13. 6}$$
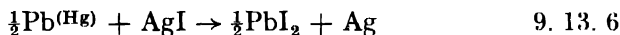
For this cell at 25 °C it is found † that

$$E = 207.8 \pm 0.2 \, \text{mV} \cdot \qquad \text{9. 13. 7}$$

$$\frac{\partial E}{\partial T} = -0.188 \pm 0.002 \, \text{mV deg}^{-1} \qquad \text{9. 13. 8}$$

The data for neither of these cells can be used directly for testing Nernst's heat theorem owing to lack of calorimetric data for PbI_2 down to low temperatures. However by subtracting (7) from (3) and (8) from (4) we obtain for a cell at 25 °C in which the cell process is

$$\text{Ag} + \text{I} \rightarrow \text{AgI} \qquad (T = 298 \, °\text{K}) \qquad \text{9. 13. 9}$$
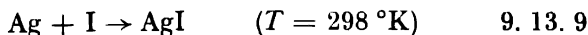
$$E = 685.8 \pm 0.2 \, \text{mV} \qquad (T = 298 \, °\text{K}) \qquad \text{9. 13. 10}$$

$$\frac{\partial E}{\partial T} = 0.146 \pm 0.004 \, \text{mV deg}^{-1} \qquad \text{9. 13. 11}$$

* Due to Webb, *J. Phys. Chem.* 1925 **29** 827.
† Gerke, *J. Amer. Chem. Soc.* 1922 **44** 1703.

Multiplying (10) and (11) by

$$F = 0.96497 \times 10^5 \text{ C mole}^{-1}$$
$$= 0.096497 \text{ kJ mV}^{-1} \text{ mole}^{-1} \qquad 9.\,13.\,12$$

and using (9. 11. 4) and (9. 12. 2), we obtain for the process (9) at 298 °K

$$\Delta G = -\ 66.17 \text{ kJ mole}^{-1} \qquad (T = 298 \text{ °K}) \quad 9.\,13.\,13$$

$$\Delta S = 14.06 \pm 0.4 \text{ J deg}^{-1} \text{ mole}^{-1} \quad (T = 298 \text{ °K}) \quad 9.\,13.\,14$$

From (13) and (14) we derive incidentally

$$\Delta H = \Delta G + T \Delta S$$
$$= (-\ 66.17 + 4.22) \text{ kJ mole}^{-1}$$
$$= -\ 61.95 \text{ kJ mole}^{-1}$$
$$= -\ 14.81 \text{ kcal mole}^{-1} \qquad 9.\,13.\,15$$

with which may be compared the calorimetrically measured value [*] $-\ 14.\ 97$ kcal mole^{-1}.

We must now convert the value of ΔS at 298 °K given by (14) to the corresponding value in the limit $T \to 0$. The following calorimetric data are available [†] for $S\,(298) - S\,(0)$.

$$\text{AgI} \quad 115.5 \pm 1.2 \text{ J deg}^{-1} \text{ mole}^{-1} \qquad 9.\,13.\,16$$

$$\text{Ag} \quad 42.5 \pm 0.4 \text{ J deg}^{-1} \text{ mole}^{-1} \qquad 9.\,13.\,17$$

$$\text{I} \quad 58.4 \text{ J deg}^{-1} \text{ mole}^{-1} \qquad 9.\,13.\,18$$

Although accurate calorimetric data for AgI are available down to $T = 15°K$, at this temperature C/R has the exceptionally high value 1.45 which leads to the rather high uncertainty, due to the extrapolation to $T = 0$, shown in (16).

Combining (16), (17) and (18) we obtain for the process (9)

$$\Delta S\,(298) - \Delta S\,(0) = 14.6 \pm 1.2 \text{ J deg}^{-1} \text{ mole}^{-1} \qquad 9.\,13.\,19$$

Now comparing (19) with (14) we obtain

$$\Delta S\,(0) = -\ 0.5 \pm 1.3 \text{ J deg}^{-1} \text{ mole}^{-1}$$

[*] Webb, *J. Phys. Chem.* 1925 **29** 827.
[†] AgI, see Pitzer, *J. Amer. Chem. Soc.* 1941 **63** 516.
Ag, see Griffiths and Griffiths, *Proc. Roy. Soc.* A 1914 **90** 557.
I, see Lange, *Z. phys. Chem.* 1924 **110** 343.
Experimental data for Ag and I recomputed by Kelley, *U. S. Bureau of Mines* 1932 Bulletin 350.

so that within the experimental accuracy $\Delta S(0) = 0$ in accordance with Nernst's heat theorem.

§ 9. 14 CELLS WITHOUT TRANSFERENCE

When an electrochemical cell contains only two solutions, one surrounding each electrode, and these two solutions are so nearly alike in composition that they be regarded as identical except with respect to the reactions at the electrodes, the cell is called a *cell without transference*. When a current flows through the cell there is in fact necessarily transference of some electrolyte from the one electrode to the other, but if the two electrode solutions are of nearly identical composition the changes in the chemical potentials of the electrolytes transferred are negligible and so this transference is without importance.

As a typical example of a *cell without transference* we again consider the cell

$$\begin{array}{cc} \text{Solution } I & \text{Solution } II \\ \text{Pt, H}_2 \quad \text{Aqueous HCl} & \text{Aqueous HCl} \quad |\text{AgCl}|\text{Ag Pt} \quad 9.\,14.\,1 \\ \text{saturated with H}_2 & \text{saturated with AgCl} \end{array}$$
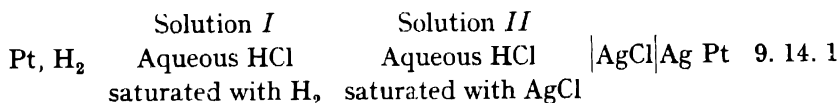
When one faraday flows from the left to the right, the following changes take place:

(a)   at the left electrode

$$\tfrac{1}{2}\text{H}_2\,(g) \rightarrow \text{H}^+\,(\text{aq } I) \qquad\qquad 9.\,14.\,2$$

(b)   at the right electrode

$$\text{AgCl}\,(s) \rightarrow \text{Ag}\,(s) + \text{Cl}^-\,(\text{aq } II) \qquad\qquad 9.\,14.\,3$$
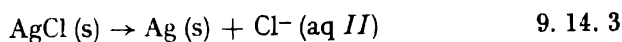
(c)   there is a simultaneous transfer of some H^+ ions from left to right and of Cl^- ions from right to left such that the net transfer of charge from left to right is one faraday and that electrical neutrality is preserved in both electrode solutions.

Since however we ignore the effect on the properties of the HCl of saturating the solution with either H_2 or AgCl, we need not distinguish between the two electrode solutions. We may therefore replace (1) by

$$\text{Pt, H}_2 \mid \text{Aqueous HCl} \mid \text{AgCl} \mid \text{Ag} \mid \text{Pt} \qquad 9.\,14.\,4$$
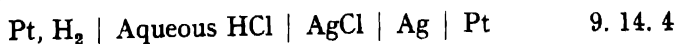
Correspondingly (a) and (b) reduce to

$$\text{(a)} \quad \tfrac{1}{2}\text{H}_2\,(g) \rightarrow \text{H}^+\,(\text{aq}) \qquad\qquad 9.\,14.\,5$$

$$\text{(b)} \quad \text{AgCl}\,(s) \rightarrow \text{Ag}\,(s) + \text{Cl}^-\,(\text{aq}) \qquad\qquad 9.\,14.\,6$$
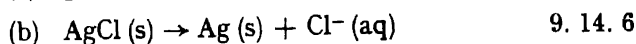
and (c) may be ignored. Thus the chemical change accompanying the flow of one faraday reduces to

$$\tfrac{1}{2}H_2\,(g) + AgCl\,(s) \rightarrow Ag\,(s) + H^+\,(aq) + Cl^-\,(aq) \qquad 9.14.7$$
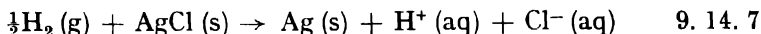
for which

$$\Delta G = \mu_{Ag}^{Ag} + \mu_{HCl} - \tfrac{1}{2}\mu_{H_2}^{G} - \mu_{AgCl}^{AgCl} \qquad 9.14.8$$

where the superscript ^{G} denotes the gas phase and μ_{HCl} denotes the chemical potential of HCl in the solution.

Substituting (8) into (9.11.4) we obtain

$$FE = -\mu_{Ag}^{Ag} - \mu_{HCl} + \tfrac{1}{2}\mu_{H_2}^{G} + \mu_{AgCl}^{AgCl} \qquad 9.14.9$$

in agreement with (9.10.23).

Explicit formulae for all cells without transference can be obtained similarly. We shall merely quote, without detailed derivation, one other example

$$\text{Pt} \left| \begin{array}{c} \text{Solution containing} \\ \text{Sn}^{2+} \text{ and Sn}^{4+} \end{array} \right| \begin{array}{c} \text{Solution containing} \\ \text{Fe}^{2+} \text{ and Fe}^{3+} \end{array} \left| \text{Pt} \right. \qquad 9.14.10$$
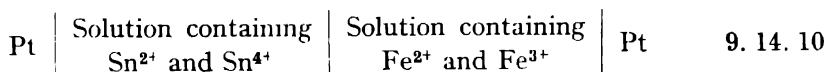
Provided that both electrode solutions contain a preponderating excess of other electrolytes and have nearly the same composition so that we may regard them as one solution, the chemical change accompanying the flow of one faraday from left to right may be written

$$\tfrac{1}{2}Sn^{2+} + Fe^{3+} \rightarrow \tfrac{1}{2}Sn^{4+} + Fe^{2+} \qquad 9.14.11$$
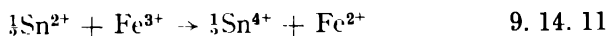
for which

$$\Delta G = \tfrac{1}{2}\mu_{Sn^{4+}} + \mu_{Fe^{2+}} - \tfrac{1}{2}\mu_{Sn^{2+}} - \mu_{Fe^{3+}} \qquad 9.14.12$$

Consequently

$$FE = \tfrac{1}{2}\mu_{Sn^{2+}} + \mu_{Fe^{3+}} - \tfrac{1}{2}\mu_{Sn^{4+}} - \mu_{Fe^{2+}}$$
$$= \tfrac{1}{2}\mu_{SnCl_2} + \mu_{FeCl_3} - \tfrac{1}{2}\mu_{SnCl_4} - \mu_{FeCl_2} \qquad 9.14.13$$

provided there is some Cl^- ion in the solutions.

§ 9.15 STANDARD ELECTROMOTIVE FORCES

Let us return to the cell described by (9.14.4) and rewrite formula (9.14.9) for its electromotive force in terms of absolute activities. We have

$$\frac{FE}{RT} = -\ln \lambda_{Ag}^{S} - \ln \lambda_{H^+} - \ln \lambda_{Cl^-} + \tfrac{1}{2}\ln \lambda_{H_2}^{G} + \ln \lambda_{AgCl}^{S} \qquad 9.15.1$$

where we have denoted the solid phase by the superscript ^{S}, the gas phase by the superscript ^{G} and the liquid phase by no superscript. Using (8. 09. 1) and (4. 21. 8) we can rewrite (1) as

$$\frac{FE}{RT} = \frac{FE^\ominus}{RT} - \ln\left(m_{H^+} m_{Cl^-} \gamma^2_{H,Cl}\right) + \tfrac{1}{2}\ln\frac{p_{H_2}}{P^\dagger} \qquad 9.\ 15.\ 2$$

where $P^\dagger$ denotes one atmosphere and $E^\ominus$ is defined by

$$\frac{FE^\ominus}{RT} = -\ln\lambda^S_{Ag} - \ln\lambda^\ominus_{H^+} - \ln\lambda^\ominus_{Cl^-} + \tfrac{1}{2}\ln\lambda^\dagger_{H_2} + \ln\lambda^S_{AgCl} \qquad 9.\ 15.\ 3$$

and is independent of the composition of the solution and independent of the pressure of the gaseous hydrogen. This quantity $E^\ominus$ is called the *standard electromotive force* of cells having the specified electrodes in the specified solvent at a specified temperature.

Similarly the electromotive force of the cell described by (9. 14. 10) can be expressed by the formula

$$\frac{FE}{RT} = \frac{FE^\ominus}{RT} - \tfrac{1}{2}\ln\frac{m_{Sn^{4+}}\,\gamma_{Sn^{4+}}}{m_{Sn^{2+}}\,\gamma_{Sn^{2+}}} + \ln\frac{m_{Fe^{3+}}\,\gamma_{Fe^{3+}}}{m_{Fe^{2+}}\,\gamma_{Fe^{2+}}} \qquad 9.\ 15.\ 4$$

in which the standard electromotive force $E^\ominus$ is defined by

$$\frac{FE^\ominus}{RT} = -\tfrac{1}{2}\ln\frac{\lambda^\ominus_{Sn^{4+}}}{\lambda^\ominus_{Sn^{2+}}} + \ln\frac{\lambda^\ominus_{Fe^{3+}}}{\lambda^\ominus_{Fe^{2+}}} \qquad 9.\ 15.\ 5$$

It can readily be verified that in all these formulae only such combinations of $\lambda^\ominus$'s and of γ's occur as satisfy the condition (8. 04. 17) with (8. 04. 18).

Formulae such as the above have two applications. Firstly by making measurements of E over a range of molalities as low as possible and extrapolation with the help of formulae such as those of §§ 8. 17—8. 22 we can obtain the value of the standard electromotive force $E^\ominus$. Secondly having determined the value of $E^\ominus$ by extrapolation we can insert this value into the formulae and so obtain information about certain combinations of activity coefficients in solutions of given composition.

§ 9. 16 NUMERICAL EXAMPLE

We shall illustrate the procedure described in the previous section by an example. We choose the cell

$$\text{Pt, H}_2 \left| \begin{array}{c} \text{Aqueous HCl} \\ \text{molality } m \end{array} \right| \text{HgCl} \left| \text{Hg} \right. \qquad 9.\,16.\,1$$
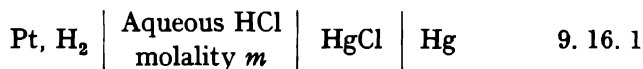
for which there exist measurements * at 25 °C of exceptionally high accuracy. The electromotive force of this cell is given by

$$E = E^{\ominus} - \frac{2RT}{F} \ln m - \frac{2RT}{F} \ln \gamma \qquad 9.\,16.\,2$$

where m is the molality and γ the mean activity coefficient of HCl. We assume that at sufficiently high dilutions γ can be represented by formula (8. 21. 5)

$$\ln \gamma = - \frac{am^{\frac{1}{2}}}{1 + m^{\frac{1}{2}}} + 2\beta m \qquad 9.\,16.\,3$$

where a has the value determined by (8. 17. 2) and β is an adjustable constant. We now define the experimental quantity $E^{\ominus\prime}$ by

$$E^{\ominus\prime} = E + \frac{2RT}{F} \ln m - \frac{2RT}{F} \frac{am^{\frac{1}{2}}}{1 + m^{\frac{1}{2}}} \qquad 9.\,16.\,4$$

Using (3) and (4) in (2) we obtain

$$E^{\ominus\prime} = E^{\ominus} - \frac{4RT}{F} \beta m \qquad 9.\,16.\,5$$

If then we plot $E^{\ominus\prime}$ against m, in so far as γ can be represented by formula (3), we shall obtain a straight line of slope $4RT\beta/F$ and of intercept at $m = 0$ equal to $E^{\ominus}$. This plot is shown in fig. 9. 1 from which we find that $E^{\ominus} = 267.96$ mV and $\beta = 0.270$ kg mole^{-1}. We further see from the diagram that with this value of β formula (3) is as accurate as the experimental measurements for all values of m up to about 0.08 mole kg^{-1}.

§ 9. 17 STANDARD ELECTROMOTIVE FORCE OF HALF-CELLS

Let us consider the three cells

$$\text{Pt, H}_2 \quad \begin{array}{c} \text{Solution} \\ \text{containing H}^+ \end{array} \quad \begin{array}{c} \text{Solution} \\ \text{containing Cl}^- \end{array} \quad \text{AgCl} \quad \text{Ag} \quad \text{Pt} \qquad 9.\,17.\,1$$
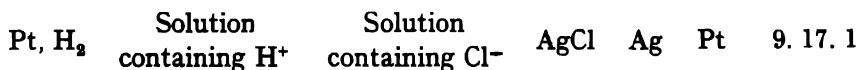
* Hills and Ives, *J. Chem. Soc.* 1951 315.
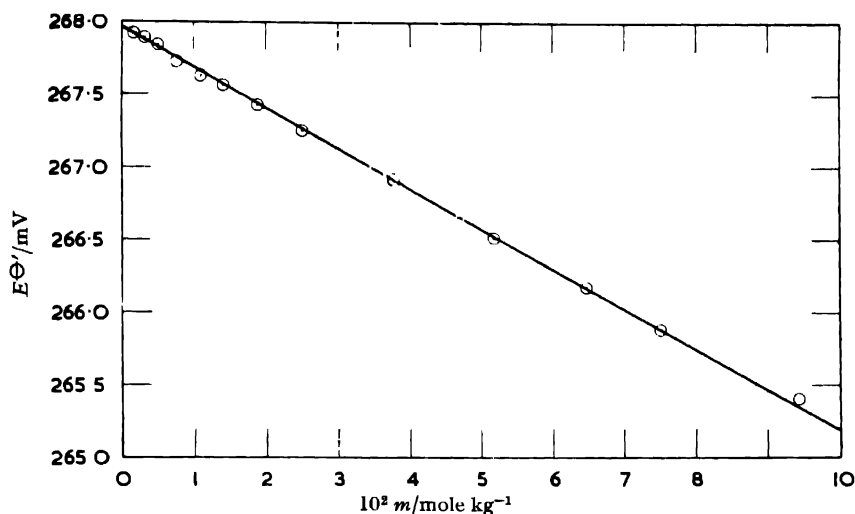
Fig 9. 1. Determination of $E^{\ominus}$ by extrapolation to $m = 0$.

$$\text{Pt, H}_2 \mid \begin{array}{c} \text{Solution} \\ \text{containing H}^+ \end{array} \quad \begin{array}{c} \text{Solution} \\ \text{containing} \\ \text{Sn}^{2+} \text{ and Sn}^{4+} \end{array} \quad \text{Pt} \qquad 9.\ 17.\ 2$$

$$\text{Pt} \quad \begin{array}{c} \text{Solution} \\ \text{containing} \\ \text{Sn}^{2+} \text{ and Sn}^{4+} \end{array} \quad \begin{array}{c} \text{Solution} \\ \text{containing Cl}^- \end{array} \quad \text{AgCl} \quad \text{Ag} \quad \text{Pt} \qquad 9.\ 17.\ 3$$
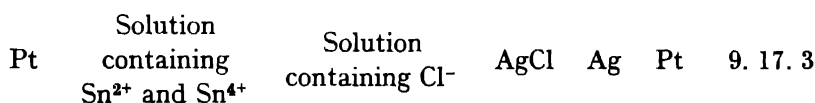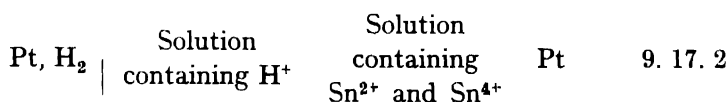
In each cell we assume that the two electrode solutions have nearly the same composition. The standard electromotive forces of the three cells are given respectively by

$$\frac{FE^{\ominus}}{RT} = \tfrac{1}{2} \ln \lambda^{\ddagger}_{\text{H}_2} - \ln \lambda^{\ominus}_{\text{H}^+} + \ln \lambda^{\text{S}}_{\text{AgCl}} - \ln \lambda^{\text{S}}_{\text{Ag}} - \ln \lambda^{\ominus}_{\text{Cl}^-} \qquad 9.\ 17.\ 4$$

$$\frac{FE^{\ominus}}{RT} = \tfrac{1}{2} \ln \lambda^{\ddagger}_{\text{H}_2} - \ln \lambda^{\ominus}_{\text{H}^+} + \tfrac{1}{2} \ln \frac{\lambda^{\ominus}_{\text{Sn}^{4+}}}{\lambda^{\ominus}_{\text{Sn}^{2+}}} \qquad 9.\ 17.\ 5$$

$$\frac{FE^{\ominus}}{RT} = - \tfrac{1}{2} \ln \frac{\lambda^{\ominus}_{\text{Sn}^{4+}}}{\lambda^{\ominus}_{\text{Sn}^{2+}}} + \ln \lambda^{\text{S}}_{\text{AgCl}} - \ln \lambda^{\text{S}}_{\text{Ag}} - \ln \lambda^{\ominus}_{\text{Cl}^-} \qquad 9.\ 17.\ 6$$

and we observe that the value of $E^{\ominus}$ for the third cell is equal to the difference between the values of $E^{\ominus}$ for the first and second cells. It is clear from this example that if there are available n different kinds of electrodes, although these can be paired to give $\tfrac{1}{2}n(n-1)$ different

cells, only $n - 1$ of these $E^{\ominus}$ values are independent. For example if we know the $E^{\ominus}$ values for all cells in which one of the electrodes is the Pt, H_2 electrode, then the $E^{\ominus}$ values of all other combinations can be obtained by adding and subtracting.

The $E^{\ominus}$ value of a cell consisting of an electrode a and a Pt, H_2 electrode is called the *standard electromotive force of the half cell a*. We recall the convention that a positive value of E means that the electrode on the right is positive. We shall now illustrate by an example how this convention is extended to the electromotive force of half cells.

We may state that the half-cell

$$\text{Cl}^- \mid \text{AgCl} \mid \text{Ag} \qquad 9.\,17.\,7$$

has $E^{\ominus} = 222.5\,\text{mV}$ at 25 °C and this means that the cell

$$\text{Pt, H}_2 \left| \begin{array}{c} \text{Solution} \\ \text{containing H}^+ \end{array} \right| \begin{array}{c} \text{Solution} \\ \text{containing Cl}^- \end{array} \left| \text{AgCl} \right| \text{Ag} \qquad 9.\,17.\,8$$
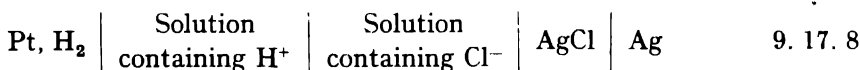
has $E^{\ominus} = 222.5$ mV with the electrode on the right positive. Alternatively we may state that the half-cell

$$\text{Ag} \mid \text{AgCl} \mid \text{Cl}^- \qquad 9.\,17.\,9$$

has $E^{\ominus} = -222.5\,\text{mV}$ at 25 °C and this means that the cell

$$\text{Ag} \left| \text{AgCl} \right| \begin{array}{c} \text{Solution} \\ \text{containing Cl}^- \end{array} \left| \begin{array}{c} \text{Solution} \\ \text{containing H}^+ \end{array} \right| \text{Pt, H}_2 \qquad 9.\,17.\,10$$
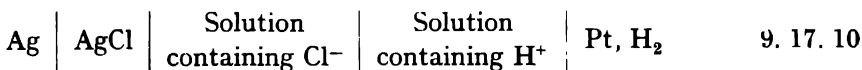
has $E^{\ominus} = -222.5$ mV with the electrode on the right negative. These conventions, which are unambiguous, have now been internationally agreed *.

§ 9. 18 CELLS WITH TRANSFERENCE WITH TWO SIMILAR ELECTRODES

Any cell which does not satisfy the conditions in the definition of a cell without transference, is called a *cell with transference*. The detailed discussion of a *cell with transference* is more involved than that of a *cell without transference*. We shall initially restrict ourselves to the case that the two electrodes are of the same chemical nature so that

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* 1953 *C. R. XVII Conf. Int. Union Pure App. Chem.* Stockholm, p. 83.

the chemical processes taking place at the electrodes are the converse of each other. For example we may consider the cell

$$\text{Ag} \mid \text{AgCl} \mid \begin{array}{c} \text{Solution } I \\ \text{containing} \\ \text{Cl}^- \end{array} \mid \begin{array}{c} \text{Bridge} \\ \text{solutions} \end{array} \mid \begin{array}{c} \text{Solution } II \\ \text{containing} \\ \text{Cl}^- \end{array} \mid \text{AgCl} \mid \text{Ag} \qquad 9.\,18.\,1$$
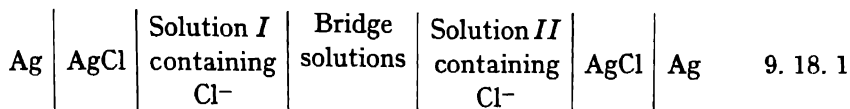
We assume that the two electrode solutions I and II are connected by *bridge solutions* in which the composition varies continuously. It is essential to exclude any discontinuity of composition, for in that case the passage of an infinitesimal current would not be reversible and it would not then be possible to apply thermodynamic equations. Suppose for example in two solutions in contact the cation Na^+ were present in that on the left but not that on the right, while the cation K^+ were present in the solution on the right but not that on the left. Then an infinitesimal current from left to right would transfer Na^+ from the left solution to the right solution. Reversal of the current would on the other hand transfer K^+ from the right solution to the left solution. If however any two solutions in contact differ only infinitesimally in composition, the passage of current will be reversible. It is true that simultaneously there is taking place an irreversible diffusion between the two solutions tending to equalize their compositions.

This condition of continuity of composition is the only condition imposed on the nature of the bridge solutions. In view of this condition the compositions of the outermost bridge solutions are identical respectively with those of the electrode solutions. If the bridge solutions are formed by natural mixing or interdiffusion of the two electrode solutions, then their compositions throughout will be intermediate between those of the two electrode solutions. On the other hand the middle portion of the bridge solutions may consist of a solution of entirely different composition from either electrode solution, but such solution must be connected to each electrode solution through solutions of continuously varying composition. The formulae which we are about to derive are applicable to all cases, but we begin by considering the more elementary cell

$$\text{Ag} \quad \text{AgCl} \quad \begin{array}{c} \text{Solution} \\ \text{molalities } m \end{array} \quad \begin{array}{c} \text{Solution} \\ \text{molalities} \\ m + dm \end{array} \mid \text{AgCl} \mid \text{Ag} \qquad 9.\,18.\,2$$
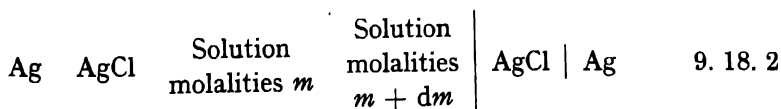
where the two electrode solutions differ only infinitesimally in composition.

Even in the elementary cell (2) there is not thermodynamic equilibrium and there is inevitably a state of interdiffusion between the two solutions. We are consequently compelled to introduce some assumption extraneous to classical thermodynamics which applies strictly only to equilibrium conditions. Initially we make the simplest, but not the least restrictive, assumption leading to correct conclusions. In chapter 14 it will be shown how the same conclusions can be reached by a less restrictive assumption. We here assume that the flow J_i per unit area per unit time of the ionic species i is directly proportional to the gradient of its electrochemical potential μ_i. We may, for simplicity and without any loss of generality in our conclusions, assume that the gradients are in the y direction. Our assumption thus becomes

$$J_i = -L_i \frac{\mathrm{d}\mu_i}{\mathrm{d}y} \qquad\qquad 9.\ 18.\ 3$$

where L_i may depend on the composition of the solution but is independent of the gradient of the composition and independent of the flow. We consider the condition of zero electric current which exists when the cell circuit is open or alternatively when the cell is exactly balanced against a potentiometer bridge. At each electrode we have the equilibrium

$$\mathrm{Cl^-} + \mathrm{Ag} \rightleftharpoons \mathrm{AgCl} + \mathrm{el^-} \qquad\qquad 9.\ 18.\ 4$$
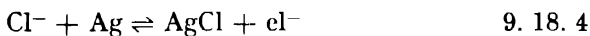
where $\mathrm{Cl^-}$ denotes chloride ion in solution and $\mathrm{el^-}$ denotes electrons in the silver. The condition for this equilibrium is

$$\frac{1}{z_{\mathrm{Cl^-}}} \mathrm{d}\mu_{\mathrm{Cl^-}} = -\mathrm{d}\mu_{\mathrm{el^-}} \qquad\qquad 9.\ 18.\ 5$$

since the silver has the same chemical potential at both ends and likewise the silver chloride. The charge number of the chloride ion is of course -1, but we have deliberately displayed it as $z_{\mathrm{Cl^-}}$ in order to facilitate generalization to other cells having electrodes reversible with respect to ions other than the chloride ion. The electromotive force $\mathrm{d}E$ of the cell (2) is then given by

$$\mathrm{F}\mathrm{d}E = -\mathrm{d}\mu_{\mathrm{el^-}} = \frac{1}{z_{\mathrm{Cl^-}}} \mathrm{d}\mu_{\mathrm{Cl^-}} \qquad\qquad 9.\ 18.\ 6$$

which we may also write as

$$\mathrm{F}\frac{\mathrm{d}E}{\mathrm{d}y} = \frac{1}{z_{\mathrm{Cl^-}}} \frac{\mathrm{d}\mu_{\mathrm{Cl^-}}}{\mathrm{d}y} \qquad\qquad 9.\ 18.\ 7$$

The condition for zero electric current is

$$\Sigma_i z_i J_i = 0 \qquad\qquad 9.\,18.\,8$$

Substituting (3) into (8) we have

$$\Sigma_i z_i L_i \frac{d\mu_i}{dy} \qquad 0 \qquad\qquad 9.\,18.\,9$$

We now multiply (7) by $\Sigma_i z_i^2 L_i$ and subtract (9) obtaining

$$\Sigma_i z_i^2 L_i \mathrm{F} \frac{dE}{dy} = \Sigma_i z_i^2 L_i \left(-\frac{1}{z_i} \frac{d\mu_i}{dy} + \frac{1}{z_{\mathrm{Cl}^-}} \frac{d\mu_{\mathrm{Cl}^-}}{dy} \right) \qquad 9.\,18.\,10$$

and consequently

$$\mathrm{F}dE = \frac{\Sigma_i z_i^2 L_i \left(-\dfrac{1}{z_i} d\mu_i + \dfrac{1}{z_{\mathrm{Cl}^-}} d\mu_{\mathrm{Cl}^-} \right)}{\Sigma_i z_i^2 L_i} \qquad 9.\,18.\,11$$

Formulae (10) and (11) in contrast to the deceptively simpler formula (7) contain only such linear combinations of $d\mu$'s as satisfy the condition for unambiguity (8. 04. 18).

Formula (11) is a complete and unambiguous formula for the electromotive force in terms of the quantities L_i defined in our assumption (3). We can however transform the expression on the right of (11) into a more perspicuous form by considering the different condition where the two electrode solutions are identical and an external potential difference dE^e is applied across the electrodes. Under these conditions we have

$$\frac{1}{z_i} d\mu_i = \mathrm{F}dE^e \qquad (\text{all } i) \qquad\qquad 9.\,18.\,12$$

Hence according to (3)

$$J_i = -z_i L_i \mathrm{F} \frac{dE^e}{dy} \qquad (\text{all } i) \qquad\qquad 9.\,18.\,13$$

and the electrical current per unit cross-section carried by the ionic species i will be

$$z_i \mathrm{F} J_i = -z_i^2 L_i \mathrm{F}^2 \frac{dE^e}{dy} \qquad\qquad 9.\,18.\,14$$

The fraction of the total current carried by the ionic species i, called the *transport number* t_i of the species i is then given by

$$t_i = \frac{z_i^2 L_i}{\Sigma_i z_i^2 L_i} \qquad 9.\,18.\,15$$

Comparing (11) with (15) we deduce

$$\mathbf{F} dE = \Sigma_i t_i \left(-\frac{1}{z_i} d\mu_i + \frac{1}{z_{Cl^-}} d\mu_{Cl^-} \right) \qquad 9.\,18.\,16$$

Returning now to cell (1) we see that this may always be regarded as several cells of type (2) in series, all electrodes other than the two extreme ones cancelling in pairs. We accordingly deduce from (16) for the electromotive force E of cell (1)

$$\mathbf{F} E = \int \Sigma_i t_i \left(-\frac{1}{z_i} d\mu_i + \frac{1}{z_{Cl^-}} d\mu_{Cl^-} \right) \qquad 9.\,18.\,17$$

where the integration extends through all the bridge solutions from the left electrode solution I to the right electrode solution II.

We can rewrite (17) in terms of absolute activities as

$$\frac{\mathbf{F} E}{RT} = \int \Sigma_i t_i \left(-\frac{1}{z_i} d \ln \lambda_i + \frac{1}{z_{Cl^-}} d \ln \lambda_{Cl^-} \right) \qquad 9.\,18\;18$$

or in terms of molalities and activity coefficients as

$$\frac{\mathbf{F} E}{RT} = \int \Sigma_i t_i \left(-\frac{1}{z_i} d \ln m_i \gamma_i + \frac{1}{z_{Cl^-}} d \ln m_{Cl^-} \gamma_{Cl^-} \right) \qquad 9.\,18.\,19$$

We again stress that only such combinations of activity coefficients occur in (19) as are, in accordance with the condition (8. 04. 18), unambiguously defined.

§ 9. 19 DETERMINATION OF TRANSPORT NUMBERS

Formula (17) gives an explicit value of the electromotive force E, but to apply it or test it we require to know the values of the transport numbers of all cations, and all anions throughout the bridge solutions. This in turn involves a knowledge of the compositions of all the continuous series of solutions forming the bridge. Since this knowledge is usually not available, formula (9. 18. 19) though exact is not of much use except in specially simple cases.

The simplest and the most useful example of a cell with transference is that in which there is only one kind of cation and one kind of anion in the whole cell. Let us consider for example the cell

$$\text{Ag} \left| \text{AgCl} \right| \begin{array}{c} \text{Aqueous MgCl}_2 \\ \text{at molality } m_1 \end{array} \left| \begin{array}{c} \text{Transition} \\ \text{layer} \end{array} \right| \begin{array}{c} \text{Aqueous MgCl}_2 \\ \text{at molality } m_2 \end{array} \left| \text{AgCl} \right| \text{Ag}$$

$$9.\ 19.\ 1$$
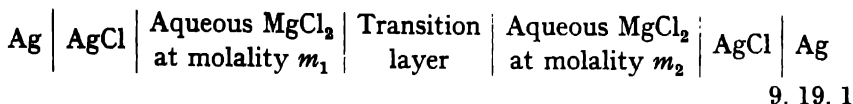
We use the name *transition layer* to denote the naturally formed bridge between the two electrode solutions consisting entirely of solutions of $MgCl_2$ of intermediate compositions. For the cell (1) formula (9. 18. 19) reduces to

$$\frac{FE}{RT} = \int_{m=m_1}^{m=m_2} - t_{Mg^{2+}} \left\{ \frac{\mathrm{d}\ln m_{Mg^{2+}} \gamma_{Mg^{2+}}}{2} - \frac{\mathrm{d}\ln m_{Cl^-} \gamma_{Cl^-}}{(-1)} \right\}$$

$$= -\tfrac{1}{2} \int_{m=m_1}^{m=m_2} t_{Mg^{2+}} \,\mathrm{d}\ln (m^3 \gamma^3_{Mg,Cl}) \qquad 9.\ 19.\ 2$$

where m denotes the molality and $\gamma_{Mg,Cl}$ the mean activity coefficient of the electrolyte $MgCl_2$.

Since in solutions containing only the single electrolyte $MgCl_2$ the value of $t_{Mg^{2+}}$ depends only on the molality, the integral in (2) is completely defined and is independent of how the molality varies along the transition layer. In particular it is independent of whether the transition layer has been formed mainly by mixing of the two electrode solutions or mainly by interdiffusion between them.

If the molalities of the two electrode solutions do not differ greatly from each other, it may be legitimate to neglect the variation of $t_{Mg^{2+}}$ with composition. In this case (2) simplifies to

$$\frac{FE}{RT} = -\tfrac{3}{2} t_{Mg^{2+}} \ln \frac{m_2 \gamma_2}{m_1 \gamma_1} \qquad 9.\ 19.\ 3$$

where γ_1, γ_2 denote the mean activity coefficients of $MgCl_2$ in solutions of molality m_1, m_2 respectively.

If the values of $\gamma_{Mg,Cl}$ are known either from measurements of the electromotive force of cells without transference or by freezing-point measurements combined with use of the Gibbs-Duhem relation, then formula (2) can be used to give information concerning the transport number $t_{Mg^{2+}}$. Conversely if there are independent measurements of this transport number, then formula (2) may be used to give information about the dependence of the mean activity coefficient $\gamma_{Mg,Cl}$ on the molality.

§ 9. 20 CELLS WITH TRANSFERENCE HAVING TWO DISSIMILAR ELECTRODES

In § 9. 14 we discussed cells without transference and in § 9. 18 cells with transference having two similar electrodes. We have still to consider cells with transference having two dissimilar electrodes. These are most easily disposed of by regarding them as a combination of the two types of cell previously discussed. This will be made clear by a typical example.

The cell

$$\text{Pt, H}_2 \left| \begin{array}{c} \text{Solution } I \\ \text{containing HCl} \end{array} \right| \begin{array}{c} \text{Bridge} \\ \text{solutions} \end{array} \left| \begin{array}{c} \text{Solution } II \\ \text{containing HCl} \end{array} \right| \text{AgCl} \left| \text{Ag} \right\| \text{Pt}$$

9. 20. 1
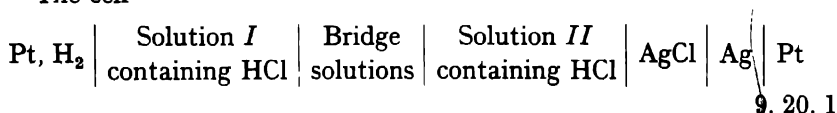
may be regarded as a combination of the two cells

$$\text{Pt, H}_2 \left| \begin{array}{c} \text{Solution } I \\ \text{containing HCl} \end{array} \right| \text{AgCl} \left| \text{Ag} \right| \text{Pt} \qquad 9. 20. 2$$

$$\text{Pt} \left| \text{Ag} \right| \text{AgCl} \left| \begin{array}{c} \text{Solution } I \\ \text{containing HCl} \end{array} \right| \begin{array}{c} \text{Bridge} \\ \text{solutions} \end{array} \left| \begin{array}{c} \text{Solution } II \\ \text{containing HCl} \end{array} \right| \text{AgCl} \left| \text{Ag} \right| \text{Pt}$$

9. 20. 3
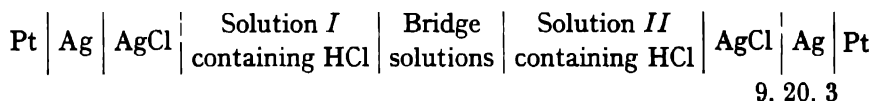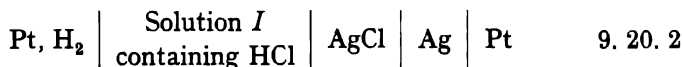
Consequently the electromotive force of the cell (1) is the sum of those of the cells (2) and (3). But cell (2) is without transference and, as shown in § 9. 14, its electromotive force E_2 is given by

$$FE_2 = -\mu_{\text{Ag}}^{\text{Ag}} + \tfrac{1}{2}\mu_{\text{H}_2}^{\text{G}} + \mu_{\text{AgCl}}^{\text{AgCl}} - \mu_{\text{HCl}}^I \qquad 9. 20. 4$$

where the superscript ^{I} refers to the solution I. Cell (3) on the other hand has two similar electrodes and its electromotive force E_3 is given by (9. 18. 17)

$$FE_3 = -\int_I^{II} \Sigma_{\text{R}}\, t_{\text{R}} \left(\frac{d\mu_{\text{R}}}{z_{\text{R}}} - \frac{d\mu_{\text{Cl}^-}}{z_{\text{Cl}^-}} \right)$$

$$\qquad\qquad - \int_I^{II} \Sigma_{\text{X}}\, t_{\text{X}} \left(\frac{d\mu_{\text{X}}}{z_{\text{X}}} - \frac{d\mu_{\text{Cl}^-}}{z_{\text{Cl}^-}} \right) \qquad 9. 20. 5$$

wherein we recall that $z_{\text{Cl}^-} = -1$ and all the z_{X} are negative integers. The electromotive force E_1 of the cell 1 is then given by

$$E_1 = E_2 + E_3 \qquad 9. 20. 6$$

The accurate expressions for the electromotive force of the most general type of cell with transference were formulated by P. B. Taylor.[*]

[*] P. B. Taylor, *J. Phys. Chem.* 1927 **31** 1478.
Cf. Guggenheim, *J. Phys. Chem.* 1930 **34** 1758.

GRAVITATIONAL FIELD

§ 10. 01 NATURE OF GRAVITATIONAL FIELD

The formulae of chapter 1 are easily extended so as to take account of the presence of a gravitational field. Such a field is characterized by a gravitational potential Φ with a definite value at each place. The modification of the gravitational field by the presence of matter in quantities of the order of magnitude of those dealt with in ordinary chemical and physical processes is completely negligible compared with the earth's field or any other field of comparable importance. We may therefore regard the gravitational field as completely independent of the state of the thermodynamic system considered. In this sense, we call the gravitational field an *external field*, and regard the gravitational potential at each point as independent of the presence or state of any matter there. It is owing to this fact that, although the abstract theories of gravitational and electrostatic potential are in many ways parallel, yet their significance for thermodynamic systems is different.

§ 10. 02 PHASES IN GRAVITATIONAL FIELD

Since a phase was defined as completely homogeneous in its properties and *state*, two portions of matter of identical temperature and composition must be considered as different phases if they are differently situated with respect to a gravitational field. It follows that the mere presence of a gravitational field excludes the possibility of a phase of finite depth in the direction of the field. In the presence of a gravitational field even the simplest possible kind of system must be considered as composed of a continuous sequence of phases each differing infinitesimally from its neighbours.

§ 10. 03 THERMODYNAMIC FUNCTIONS IN GRAVITATIONAL FIELD

The characteristic property of the gravitional potential is that the work w required to bring a quantity of matter of mass M from a place where the potential is Φ^α to a place where it is Φ^β is given by

$$w = M \left(\Phi^\beta - \Phi^\alpha \right) \qquad \text{10. 03. 1}$$

thus depending on the mass but not on the chemical nature of the matter. If the molar mass of the species i is denoted by M_i and the number of moles of this species transferred is v_i, then (1) becomes

$$w = \Sigma_i v_i M_i (\Phi^\beta - \Phi^\alpha) \qquad 10.\,03.\,2$$

In transferring dn_i moles of the species i from the phase α to the phase β, the gravitational work is

$$(\Phi^\beta - \Phi^\alpha)\, M_i\, dn_i$$

Thus the formula (1. 33. 1) for dU^α must for each phase α contain the extra terms $\Sigma_i \Phi^\alpha M_i\, dn_i^\alpha$. That is to say

$$dU^\alpha = T^\alpha\, dS^\alpha - P^\alpha\, dV^\alpha + \Sigma_i (\mu_i^\alpha + M_i \Phi^\alpha)\, dn_i^\alpha \qquad 10.\,03.\,3$$

For the other characteristic functions H, F and G, defined respectively by (1. 31. 1), (1. 31. 2), (1. 31. 3) we have

$$dH^\alpha = \quad T^\alpha\, dS^\alpha + V^\alpha\, dP^\alpha + \Sigma_i (\mu_i^\alpha + M_i \Phi^\alpha)\, dn_i^\alpha \qquad 10.\,03.\,4$$

$$dF^\alpha = - S^\alpha\, dT^\alpha - P^\alpha\, dV^\alpha + \Sigma_i (\mu_i^\alpha + M_i \Phi^\alpha)\, dn_i^\alpha \qquad 10.\,03.\,5$$

$$dG^\alpha = - S^\alpha\, dT^\alpha + V^\alpha\, dP^\alpha + \Sigma_i (\mu_i^\alpha + M_i \Phi^\alpha)\, dn_i^\alpha \qquad 10.\,03.\,6$$

It follows that to take account of the effect of a gravitational field one has merely to replace μ^α throughout by $(\mu_i^\alpha + M_i \Phi^\alpha)$.

Although in all thermodynamic formulae the quantity Φ^α occurs only in combinations of the form $(\mu_i^\alpha + M_i \Phi^\alpha)$, yet the gravitational potential difference $\Delta\Phi$ between two phases, in contrast to the electric potential difference $\Delta\psi$, is thermodynamically determinate owing to the fact that its value is independent of the presence and nature of the phase there. The phase may therefore be removed without altering Φ and then $\Delta\Phi$ can be determined in empty space by direct mechanical measurements.

§ 10. 04 EQUILIBRIUM IN GRAVITATIONAL FIELD

For the equilibrium as regards the species i between two phases α and β, defined not merely by their temperature, pressure and composition, but also by their gravitational potentials, we have in analogy with (1. 45. 5) the general condition

$$\mu_i^\alpha + M_i \Phi^\alpha = \mu_i^\beta + M_i \Phi^\beta \qquad \text{(equilibrium)} \qquad 10.\,04.\,1$$

§ 10. 05 DEPENDENCE OF μ_i ON T AND P

Applying the cross-differentiation identity (3. 01. 7) to (10. 03. 6), observing that M_i and Φ^a are independent of T^a and P^a, we obtain, dropping the superscript a throughout,

$$\frac{\partial \mu_i}{\partial T} = -\frac{\partial S}{\partial n_i} = -S_i \qquad 10.\,05.\,1$$

$$\frac{\partial \mu_i}{\partial P} = \frac{\partial V}{\partial n_i} = V_i \qquad 10.\,05.\,2$$

precisely the same as in the absence of a gravitational field.

§ 10. 06 SINGLE COMPONENT IN GRAVITATIONAL FIELD

For the equilibrium of a single component i in a gravitational field we have according to (10. 04. 1)

$$d\mu_i + M_i\, d\Phi = 0 \qquad 10.\,06.\,1$$

or at constant temperature using (10. 05. 2)

$$V_i\, dP + M_i\, d\Phi = 0 \qquad 10.\,06.\,2$$

If ϱ denotes the density, then

$$\varrho = \frac{M_i}{V_i} \qquad 10.\,06.\,3$$

Substituting (3) into (2) we obtain

$$dP = -\varrho\, d\Phi \qquad 10.\,06.\,4$$

in agreement with the general condition of hydrostatic equilibrium.

In the case of a single perfect gas we have

$$V_i = RT/P \qquad 10.\,06.\,5$$

Substituting (5) into (2) we obtain

$$RT\, d\ln P + M_i\, d\Phi = 0 \qquad 10.\,06.\,6$$

and by integration

$$RT\, \ln\frac{P^\beta}{P^a} = M_i\,(\Phi^a - \Phi^\beta) \qquad 10.\,06.\,7$$

For a liquid, on the other hand, neglecting compressibility and so

treating V_i as independent of P, we can integrate (2) immediately obtaining

$$V_i (P^\beta - P^\alpha) = M_i (\Phi^\alpha - \Phi^\beta) \qquad 10.\,06.\,8$$

Alternatively integrating (4) we obtain

$$P^\beta - P^\alpha = \varrho (\Phi^\alpha - \Phi^\beta) \qquad 10.\,06.\,9$$

§ 10. 07 MIXTURE IN GRAVITATIONAL FIELD

For the equilibrium of each species i of a mixture in a gravitational field we have according to (10. 04. 1)

$$d\mu_i + M_i \, d\Phi = 0 \qquad 10.\,07.\,1$$

Substituting (10. 05. 2) and using the notation defined in § 5. 03, we obtain at constant temperature

$$D\mu_i + V_i \, dP + M_i \, d\Phi = 0 \qquad 10.\,07.\,2$$

But according to the Gibbs-Duhem relation (5. 11. 4) we have

$$\Sigma_i \, x_i \, D\mu_i = 0 \qquad 10.\,07.\,3$$

Multiplying (2) by x_i, summing over all species i and using (3) we obtain

$$\Sigma_i \, x_i V_i \, dP + \Sigma_i \, x_i \, M_i \, d\Phi = 0 \qquad 10.\,07.\,4$$

Introducing the mean molar volume V_m and the mean molar mass M_m defined respectively by

$$V_m = \Sigma_i \, x_i V_i \qquad 10.\,07.\,5$$

$$M_m = \Sigma_i \, x_i M_i \qquad 10.\,07.\,6$$

we can write (4) as

$$V_m \, dP + M_m \, d\Phi = 0 \qquad 10.\,07.\,7$$

But the density ϱ is related to V_m, M_m, by

$$\varrho = M_m / V_m \qquad 10.\,07.\,8$$

Substituting (8) into (7), we recover the ordinary condition of hydrostatic equilibrium

$$dP = - \varrho \, d\Phi \qquad 10.\,07.\,9$$

If we substitute for dP from (4) into (2), we obtain

$$D\mu_i + \left(M_i - V_i \frac{\Sigma_k \, x_k M_k}{\Sigma_k \, x_k V_k} \right) d\Phi = 0 \qquad 10.\,07.\,10$$

or, according to (5) and (6),

$$D\mu_i + \left(M_i - \varrho V_i\right) d\Phi = 0 \qquad 10.\,07.\,11$$

The differential equations of this section can be integrated only in certain exceptionally simple cases which we shall consider in turn.

§ 10. 08 MIXTURE OF PERFECT GASES

For a mixture of perfect gases it is possible to integrate (10. 07. 1), but the same result can be obtained more directly. For any component i in two perfect gaseous mixtures α, β at the same temperature T, according to (5. 17. 2)

$$\mu_i^\beta - \mu_i^\alpha = RT \ln \frac{p_i^\beta}{p_i^\alpha} \qquad 10.\,08.\,1$$

Substituting (1) into (10. 04. 1) we obtain as the equilibrium condition for the species i in a gravitational field

$$RT \ln \frac{p_i^\beta}{p_i^\alpha} = M_i \left(\Phi^\alpha - \Phi^\beta\right) \qquad 10.\,08.\,2$$

or

$$\frac{p_i^\beta}{p_i^\alpha} = \exp \left\{- \frac{M_i \left(\Phi^\beta - \Phi^\alpha\right)}{RT} \right\} \qquad 10.\,08.\,3$$

If we differentiate (2) we obtain

$$\frac{dp_i}{p_i} = - \frac{M_i}{RT} d\Phi \qquad 10.\,08.\,4$$

Using

$$p_i = x_i \frac{RT}{V_m} \qquad 10.\,08.\,5$$

we can write (4) as

$$dp_i = - \frac{x_i M_i}{V_m} d\Phi \qquad 10.\,08.\,6$$

Summing (6) over all species i, we obtain

$$dP = - \frac{M_m}{V_m} d\Phi = - \varrho \, d\Phi \qquad 10.\,08.\,7$$

thus verifying that (2) and (3) are consistent with hydrostatic equilibrium.

§ 10. 09 IDEAL DILUTE SOLUTION

In the case of an ideal dilute solution we may replace (10. 07. 11) for each solute species s by

$$RT\, d \ln m_s + \left(M_s - V_s \frac{M_m}{V_m}\right) d\Phi = 0 \qquad 10.\,09.\,1$$

If the solution is also *extremely dilute* so that $\Sigma_s x_s \ll 1$ we may replace M_m/V_m by M_1/V_1^0, where the superscript ^{0} relates to the pure solvent, and obtain

$$RT\, d \ln m_s + \left(M_s - V_s \frac{M_1}{V_1^0}\right) d\Phi = 0 \qquad 10.\,09.\,2$$

Neglecting compressibility, this can be directly integrated, giving

$$\frac{m_s^\beta}{m_s^\alpha} = \exp\left\{-\left(M_s - V_s \frac{M_1}{V_1^0}\right)\frac{\Phi^\beta - \Phi^\alpha}{RT}\right\} \qquad 10.\,09.\,3$$

§ 10. 10 BINARY IDEAL MIXTURE

For an ideal mixture

$$\mathcal{D}\mu_i = RT\, d \ln x_i \qquad 10.\,10.\,1$$

and (10. 07. 10) becomes

$$RT\, d \ln x_i + \left(M_i - V_i \frac{\Sigma_k x_k M_k}{\Sigma_k x_k V_k}\right) d\Phi = 0 \qquad 10.\,10.\,2$$

This can be integrated in the special case of only two components.] we denote these components by 1 and 2, then (2) becomes

$$-\frac{d\Phi}{RT} = \frac{dx_2}{x_2}\, \frac{x_1 V_1 + x_2 V_2}{M_2(x_1 V_1 + x_2 V_2) - V_2(x_1 M_1 + x_2 M_2)}$$

$$= \frac{dx_2}{x_2}\, \frac{x_1 V_1 + x_2 V_2}{x_1(M_2 V_1 - M_1 V_2)}$$

$$= \frac{dx_2}{M_2 V_1 - M_1 V_2}\left(\frac{V_1}{x_2} - \frac{V_2}{x_1}\right)$$

$$= \frac{dx_2}{M_2 V_1 - M_1 V_2}\left(\frac{V_1}{x_2} - \frac{V_2}{1 - x_2}\right) \qquad 10.\,10.\,3$$

Since in an ideal mixture V_1, V_2 are independent of x_2, integration of (3) gives

$$-\left(M_2 - V_2 \frac{M_1}{V_1}\right) \frac{\Phi^\beta - \Phi^\alpha}{RT} = \ln \frac{x_2^\beta}{x_2^\alpha} + \frac{V_2}{V_1} \ln \frac{1 - x_2^\beta}{1 - x_2^\alpha} \qquad 10.\,10.\,4$$

or

$$\exp\left\{-\left(M_2 - V_2 \frac{M_1}{V_1}\right) \frac{\Phi^\beta - \Phi^\alpha}{RT}\right\} = \frac{x_2^\beta}{x_2^\alpha} \left(\frac{x_1^\beta}{x_1^\alpha}\right)^{V_2/V_1} \qquad 10.\,10.\,5$$

The relation (5) can also be written in the more symmetrical form

$$\exp\left\{(M_1 V_2 - M_2 V_1) \frac{\Phi^\beta - \Phi^\alpha}{RT}\right\} = \left(\frac{x_2^\beta}{x_2^\alpha}\right)^{V_1} \left(\frac{x_1^\beta}{x_1^\alpha}\right)^{V_2} \qquad 10.\,10.\,6$$

If the solution is extremely dilute with respect to the species 2, so that $x_2 \ll 1$, we may replace (5) by the approximation

$$\exp\left\{-\left(M_2 - V_2 \frac{M_1}{V_1}\right) \frac{\Phi^\beta - \Phi^\alpha}{RT}\right\} = \frac{x_2^\beta}{x_2^\alpha} = \frac{m_2^\beta}{m_2^\alpha} \qquad 10.\,10.\,7$$

in agreement with (10. 09. 3).

§ 10. 11 CHEMICAL REACTION IN GRAVITATIONAL FIELD
For the chemical reaction

$$\Sigma \nu_A\,A \to \Sigma \nu_B\,B \qquad 10.\,11.\,1$$

the most general form for the condition of equilibrium in the absence of a gravitational field is

$$\Sigma \nu_A \mu_A = \Sigma \nu_B \mu_B \qquad 10.\,11.\,2$$

In the presence of a gravitational field the corresponding equilibrium condition is evidently

$$\Sigma \nu_A (\mu_A + M_A \Phi) = \Sigma \nu_B (\mu_B + M_B \Phi) \qquad 10.\,11.\,3$$

But owing to the conservation of mass

$$\Sigma \nu_A M_A = \Sigma \nu_B M_B \qquad 10.\,11.\,4$$

Multiplying (4) by Φ and subtracting from (3) we recover (2). It follows that any chemical equilibrium constant is independent of the gravitational potential or in other words is unaffected by the presence of a gravitational field.

§ 10. 09 IDEAL DILUTE SOLUTION

In the case of an ideal dilute solution we may replace (10. 07. 11) for each solute species s by

$$RT \, \mathrm{d} \ln m_s + \left(M_s - V_s \frac{M_m}{V_m} \right) \mathrm{d}\Phi = 0 \qquad 10.\,09.\,1$$

If the solution is also *extremely dilute* so that $\Sigma_s x_s \ll 1$ we may replace M_m/V_m by M_1/V_1^0, where the superscript ^{0} relates to the pure solvent, and obtain

$$RT \, \mathrm{d} \ln m_s + \left(M_s - V_s \frac{M_1}{V_1^0} \right) \mathrm{d}\Phi = 0 \qquad 10.\,09.\,2$$

Neglecting compressibility, this can be directly integrated, giving

$$\frac{m_s^\beta}{m_s^\alpha} = \exp \left\{ - \left(M_s - V_s \frac{M_1}{V_1^0} \right) \frac{\Phi^\beta - \Phi^\alpha}{RT} \right\} \qquad 10.\,09.\,3$$

§ 10. 10 BINARY IDEAL MIXTURE

For an ideal mixture

$$\mathrm{D}\mu_i = RT \, \mathrm{d} \ln x_i \qquad 10.\,10.\,1$$

and (10. 07. 10) becomes

$$RT \, \mathrm{d} \ln x_i + \left(M_i - V_i \frac{\Sigma_k x_k M_k}{\Sigma_k x_k V_k} \right) \mathrm{d}\Phi = 0 \qquad 10.\,10.\,2$$

This can be integrated in the special case of only two components. If we denote these components by 1 and 2, then (2) becomes

$$\frac{\mathrm{d}\Phi}{RT} = \frac{\mathrm{d}x_2}{x_2} \frac{x_1 V_1 + x_2 V_2}{M_2 (x_1 V_1 + x_2 V_2) - V_2 (x_1 M_1 + x_2 M_2)}$$

$$= \frac{\mathrm{d}x_2}{x_2} \frac{x_1 V_1 + x_2 V_2}{x_1 (M_2 V_1 - M_1 V_2)}$$

$$= \frac{\mathrm{d}x_2}{M_2 V_1 - M_1 V_2} \left(\frac{V_1}{x_2} - \frac{V_2}{x_1} \right)$$

$$= \frac{\mathrm{d}x_2}{M_2 V_1 - M_1 V_2} \left(\frac{V_1}{x_2} - \frac{V_2}{1 - x_2} \right) \qquad 10.\,10.\,3$$

Since in an ideal mixture V_1, V_2 are independent of x_2, integration of (3) gives

$$-\left(M_2 - V_2 \frac{M_1}{V_1}\right)\frac{\Phi^\beta - \Phi^\alpha}{RT} = \ln\frac{x_2^\beta}{x_2^\alpha} + \frac{V_2}{V_1}\ln\frac{1 - x_2^\beta}{1 - x_2^\alpha} \qquad 10.\,10.\,4$$

or

$$\exp\left\{-\left(M_2 - V_2\frac{M_1}{V_1}\right)\frac{\Phi^\beta - \Phi^\alpha}{RT}\right\} = \frac{x_2^\beta}{x_2^\alpha}\left(\frac{x_1^\beta}{x_1^\alpha}\right)^{V_2/V_1} \qquad 10.\,10.\,5$$

The relation (5) can also be written in the more symmetrical form

$$\exp\left\{(M_1 V_2 - M_2 V_1)\frac{\Phi^\beta - \Phi^\alpha}{RT}\right\} = \left(\frac{x_2^\beta}{x_2^\alpha}\right)^{V_1}\left(\frac{x_1^\beta}{x_1^\alpha}\right)^{V_2} \qquad 10.\,10.\,6$$

If the solution is extremely dilute with respect to the species 2, so that $x_2 \ll 1$, we may replace (5) by the approximation

$$\exp\left\{-\left(M_2 - V_2\frac{M_1}{V_1}\right)\frac{\Phi^\beta - \Phi^\alpha}{RT}\right\} = \frac{x_2^\beta}{x_2^\alpha} = \frac{m_2^\beta}{m_2^\alpha} \qquad 10.\,10.\,7$$

in agreement with (10. 09. 3).

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For the chemical reaction

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the most general form for the condition of equilibrium in the absence of a gravitational field is

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In the presence of a gravitational field the corresponding equilibrium condition is evidently

$$\Sigma \nu_A (\mu_A + M_A \Phi) = \Sigma \nu_B (\mu_B + M_B \Phi) \qquad 10.\,11.\,3$$

But owing to the conservation of mass

$$\Sigma \nu_A M_A = \Sigma \nu_B M_B \qquad 10.\,11.\,4$$

Multiplying (4) by Φ and subtracting from (3) we recover (2). It follows that any chemical equilibrium constant is independent of the gravitational potential or in other words is unaffected by the presence of a gravitational field.

ELECTROSTATIC SYSTEMS

§ 11. 01 INTRODUCTION

We now propose to study the thermodynamic properties of substances in an electrostatic field. For this purpose it will suffice to consider the field in a parallel plate condenser neglecting any edge effect. Thus when we refer to the extensive properties of a parallel plate condenser of area A, we really mean the difference between those of a condenser of area $\mathcal{A} + A$ and those of a similar condenser of area $\mathcal{A}$, where $\mathcal{A} \gg A$.

As it is important to be completely unambiguous concerning the meaning of such quantities as *dielectric constant*, it is desirable to describe in some detail the characteristics of a parallel plate condenser, beginning with one in vacuo.

§ 11. 02 PARALLEL PLATE CONDENSER IN VACUO

Consider a parallel plate condenser of area A, the distance between the plates being l. Let the charges on the two plates be $+Q$ and $-Q$. The condenser being in vacuo let the work required to transfer an elementary charge dQ from the negative plate to the positive plate be $\Delta \psi \, dQ$. Then $\Delta \psi$ is called the *potential difference* between the two plates and $\mathbf{E} = \Delta \psi / l$ is called the *electric field strength* between the plates. Then the ratio ε_0 defined by

$$\frac{lQ}{A \, \Delta \psi} = \frac{Q}{A \mathbf{E}} = \frac{\varepsilon_0}{4\pi} \qquad \text{11. 02. 1}$$

is a universal constant called the *permittivity of empty space*. The value of ε_0 in various units is *

$$\varepsilon_0 = 1 \text{ franklin}^2 \text{ erg}^{-1} \text{ cm}^{-1}$$
$$= 1.113 \times 10^{-10} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$$
$$= 1.113 \times 10^{-10} \text{ C V}^{-1} \text{ m}^{-1}$$

* The name *franklin* is used for a charge which repels a similar charge at a distance one centimetre in vacuo with a force of one dyne. See *Nature* 1941 **148** 751.

§ 11. 03 PARALLEL PLATE CONDENSER IN FLUID

Now consider the same parallel plate condenser completely immersed in a homogeneous fluid. If the charges on the plates are again $+Q$ and $-Q$, and if the potential difference between the plates, defined as before is again denoted by $\Delta \psi$ then the ratio ε, defined by

$$\frac{lQ}{A \Delta \psi} = \frac{Q}{A\mathbf{E}} = \frac{\varepsilon}{4\pi} \qquad \text{11. 03. 1}$$

is called the *permittivity of the fluid*. The value of ε depends on the nature of the fluid, on its temperature and possibly also on $\mathbf{E} = \Delta \psi / l$, but is independent of the size and shape of the condenser. ε has of course the same dimensions as ε_0. The ratio $\varepsilon / \varepsilon_0$ is called the *relative permittivity* or the *dielectric coefficient* of the fluid.

§ 11. 04 WORK OF CHARGING A CONDENSER

According to (11. 03. 1) we have

$$\Delta \psi = \frac{4\pi}{\varepsilon} \frac{lQ}{A} \qquad \text{11. 04. 1}$$

and so the work required to bring an element of charge dQ from the negative to the positive plate is

$$\frac{4\pi}{\varepsilon} \frac{lQ \, dQ}{A} \qquad \text{11. 04. 2}$$

From (11. 03. 1) we have also

$$Q = \frac{A}{4\pi} \varepsilon \mathbf{E} \qquad \text{11. 04. 3}$$

$$dQ = \frac{A}{4\pi} d(\varepsilon \mathbf{E}) \qquad \text{11. 04. 4}$$

Substituting (3) and (4) into (2) we obtain for the work w required to increase the field strength from $\mathbf{E}$ to $\mathbf{E} + d\mathbf{E}$

$$w = \frac{Al}{4\pi} \mathbf{E} \, d(\varepsilon \mathbf{E}) \qquad \frac{V_c}{4\pi} \mathbf{E} \, d(\varepsilon \mathbf{E}) \qquad \text{11. 04. 5}$$

where V_c denotes the volume between the plates of the condenser and is assumed independent of temperature and pressure.

Formula (5) is valid for any infinitesimal change, including in particular an adiabatic charge and an isothermal change, but the

dependence of $\varepsilon \mathbf{E}$ on $\mathbf{E}$ will in general not be the same in these two cases. The quantity $\varepsilon \mathbf{E}$ is called the *electric displacement*.

§ 11. 05 CHARACTERISTIC FUNCTIONS

If we now consider the system consisting of the whole fluid of volume V surrounding and including the condenser, we obtain by using (11. 04. 5) the relations

$$dU = TdS - PdV + \frac{V_c}{4\pi} \mathbf{E} \, d(\varepsilon \mathbf{E}) + \Sigma_i \, \mu_i \, dn_i \qquad 11.\ 05.\ 1$$

$$dF = - SdT - PdV + \frac{V_c}{4\pi} \mathbf{E} \, d(\varepsilon \mathbf{E}) + \Sigma_i \, \mu_i \, dn_i \qquad 11.\ 05.\ 2$$

Formulae (1) and (2) are the extensions of (1. 33. 1), (1. 33. 2) respectively including the extra term (11. 04. 5) representing the work required to change the field $\mathbf{E}$ between the plates of the condenser.

We now define characteristic functions G, $\mathcal{I}$ and $\mathcal{D}$ by

$$G = F + PV \qquad 11.\ 05.\ 3$$

$$\mathcal{I} = F - \frac{V_c}{4\pi} \varepsilon \mathbf{E}^2 \qquad 11.\ 05.\ 4$$

$$\mathcal{D} = F + PV - \frac{V_c}{4\pi} \varepsilon \mathbf{E}^2 \qquad 11.\ 05.\ 5$$

When the field $\mathbf{E}$ vanishes $\mathcal{I}, \mathcal{D}$ become identical with F, G respectively.

Differentiating (3), (4) and (5) in turn and eliminating dF by means of (2), we obtain

$$dG = - SdT + VdP + \frac{V_c}{4\pi} \mathbf{E} \, d(\varepsilon \mathbf{E}) + \Sigma_i \, \mu_i \, dn_i \qquad 11.\ 05.\ 6$$

$$d\mathcal{I} = - SdT - PdV - \frac{V_c}{4\pi} \varepsilon \mathbf{E} \, d\mathbf{E} + \Sigma_i \mu_i dn_i \qquad 11.\ 05.\ 7$$

$$d\mathcal{D} = - SdT + VdP - \frac{V_c}{4\pi} \varepsilon \mathbf{E} \, d\mathbf{E} + \Sigma_i \, \mu_i \, dn_i \qquad 11.\ 05.\ 8$$

In all the above formulae P denotes the pressure acting on the outside boundary of the fluid in which the condenser is completely immersed. We have carefully avoided reference to any pressure within the fluid between the plates of the condenser, for the definition of such a pressure would require special caution and its use as an independent variable would lead to more complicated formulae.

§ 11. 06 ANALOGUES OF MAXWELL'S RELATIONS

By applying the cross-differentiation identity (3. 01. 7) to (11.05.2), (11. 05. 6), (11. 05. 7) and (11. 05. 8) we can obtain several relations analogous to Maxwell's relations obtained in § 3. 04.

Thus

$$\left(\frac{\partial S}{\partial [\varepsilon E]}\right)_{T,V} = -\frac{V_c}{4\pi}\left(\frac{\partial E}{\partial T}\right)_{V,[\varepsilon E]} = -\frac{V_c}{4\pi}\varepsilon E\left(\frac{\partial [1/\varepsilon]}{\partial T}\right)_{V,[\varepsilon E]} \qquad 11.\ 06.\ 1$$

$$\left(\frac{\partial S}{\partial [\varepsilon E]}\right)_{T,P} = -\frac{V_c}{4\pi}\left(\frac{\partial E}{\partial T}\right)_{P,[\varepsilon E]} = -\frac{V_c}{4\pi}\varepsilon E\left(\frac{\partial [1/\varepsilon]}{\partial T}\right)_{P,[\varepsilon E]} \qquad 11.\ 06.\ 2$$

$$\left(\frac{\partial S}{\partial E}\right)_{T,V} = \frac{V_c}{4\pi}\left(\frac{\partial [\varepsilon E]}{\partial T}\right)_{V,E} = \frac{V_c}{4\pi}E\left(\frac{\partial \varepsilon}{\partial T}\right)_{V,E} \qquad 11.\ 06.\ 3$$

$$\left.\frac{\partial S}{\partial E}\right)_{T,P} = \frac{V_c}{4\pi}\left(\frac{\partial [\varepsilon E]}{\partial T}\right)_{P,E} = \frac{V_c}{4\pi}E\left(\frac{\partial \varepsilon}{\partial T}\right)_{P,E} \qquad 11.\ 06.\ 4$$

Similarly we obtain

$$\left.\frac{\partial V}{\partial [\varepsilon E]}\right)_{T,P} = \frac{V_c}{4\pi}\left(\frac{\partial E}{\partial P}\right)_{T,[\varepsilon E]} = \frac{V_c}{4\pi}\varepsilon E\left(\frac{\partial [1/\varepsilon]}{\partial P}\right)_{T,[\varepsilon E]} \qquad 11.\ 06.\ 5$$

$$\left.\frac{\partial V}{\partial E}\right)_{T,P} = -\frac{V_c}{4\pi}\left(\frac{\partial [\varepsilon E]}{\partial P}\right)_{T,E} = -\frac{V_c}{4\pi}E\left(\frac{\partial \varepsilon}{\partial P}\right)_{T,E} \qquad 11.\ 06.\ 6$$

This change in volume accompanying change in field strength at constant temperature and pressure is called *electrostriction*.

§ 11. 07 CONSTANT PERMITTIVITY. DIELECTRIC CONSTANT

For the sake of generality we have hitherto made no assumption concerning the dependence of the permittivity ε on the field strength **E**. For almost all substances at field strengths met in an ordinary laboratory the permittivity ε is for a given temperature and pressure independent of the field strength. We shall from here onwards assume this to be case. The *dielectric coefficient* $\varepsilon/\varepsilon_0$ is then called the *dielectric constant*.

Both formulae (11. 06. 1) and (11. 06. 3) now reduce to

$$\left(\frac{\partial S}{\partial \mathbf{E}}\right)_{T,V} = \frac{V_c}{4\pi}\,\mathbf{E}\left(\frac{\partial \varepsilon}{\partial T}\right)_V \qquad \text{11. 07. 1}$$

while formulae (11. 06. 2) and (11. 06. 4) both reduce to

$$\left(\frac{\partial S}{\partial \mathbf{E}}\right)_{T,P} = \frac{V_c}{4\pi}\,\mathbf{E}\left(\frac{\partial \varepsilon}{\partial T}\right)_P \qquad \text{11. 07. 2}$$

The electrostriction formulae (11. 06. 5) and (11. 06. 6) both reduce to

$$\left(\frac{\partial V}{\partial \mathbf{E}}\right)_{T,P} = -\frac{V_c}{4\pi}\,\mathbf{E}\left(\frac{\partial \varepsilon}{\partial P}\right)_T \qquad \text{11. 07. 3}$$

§ 11. 08 INTEGRATED FORMULAE

If we assume that ε is independent of $\mathbf{E}$, we can integrate (11. 05. 2) at constant T, V, n_i obtaining

$$F = F^0 + V_c\,\frac{\varepsilon \mathbf{E}^2}{8\pi} \qquad \text{11. 08. 1}$$

where F^0 denotes the value of the free energy, at zero field and at the given temperature and total volume.

We may note that the quantity $\varepsilon \mathbf{E}^2/8\pi$ which in textbooks on electricity is usually described as the energy density due to the field, is in fact the *free energy density*.

From (1) we deduce for the energy U using (11. 07. 1),

$$U = F + TS = U^0 + V_c\,\frac{\mathbf{E}^2}{8\pi}\left(\varepsilon + T\,\frac{d\varepsilon}{dT}\right) \qquad \text{11. 08. 2}$$

where U^0 denotes the value of the energy, at zero field and at the given temperature and total volume. We thus see that the *energy density* due to the field is

$$\frac{\mathbf{E}^2}{8\pi}\left(\varepsilon + T\,\frac{d\varepsilon}{dT}\right) \qquad \text{11. 08. 3}$$

To obtain a formula for μ_i according to (11. 05. 2) we differentiate (1)

with respect to n_i at constant T, V and $\varepsilon \mathbf{E}$. We thus find when ε is independent of $\mathbf{E}$

$$\mu_i = \mu_i^0 + \frac{V}{8\pi} \left(\frac{\partial [\varepsilon \mathbf{E}^2]}{\partial n_i} \right)_{T, V, [\varepsilon \mathbf{E}]}$$

$$= \mu_i^0 + \frac{V \varepsilon^2 \mathbf{E}^2}{8\pi} \left(\frac{\partial [1/\varepsilon]}{\partial n_i} \right)_{T, V}$$

$$= \mu_i^0 - V \frac{\mathbf{E}^2}{8\pi} \left(\frac{\partial \varepsilon}{\partial n_i} \right)_{T, V} \qquad 11.\,08.\,4$$

where μ_i^0 denotes the value of μ_i at zero field strength and at the same temperature and composition.

§ 11. 09 APPLICATION TO PERFECT GAS

We shall illustrate the use of the relation (11. 08. 4) by its application to the simplest case of a single perfect gas.

The permittivity ε of a perfect gas is related to the permittivity ε_0 of free space by

$$\frac{\varepsilon - \varepsilon_0}{4\pi} = \frac{n}{V} \left(a + \frac{\beta}{T} \right) \qquad 11.\,09.\,1$$

where a and β are constants characteristic of the molecules of the gas. a is equal to the molecular polarizability multiplied by Avogadro's number, while β is given by

$$\beta = \frac{L\mu^2}{3k} = \frac{(L\mu)^2}{3R} \qquad 11.\,09.\,2$$

where μ is the electric moment of the molecule, L is Avogadro's number and k is Boltzmann's constant.

Substituting (1) into (11. 08. 4) we obtain

$$\mu = \mu^0 - \tfrac{1}{2}\mathbf{E}^2 \left(a + \frac{\beta}{T} \right)$$

$$= \mu^\dagger + RT \ln \frac{nRT}{P^\dagger V} - \tfrac{1}{2}\mathbf{E}^2 \left(a + \frac{\beta}{T} \right) \qquad 11.\,09.\,3$$

using (4. 25. 2).

Let us now consider the equilibrium distribution of a gas between the region, denoted by the superscript [1], inside the condenser where the field strength is $\mathbf{E}$ and the region, denoted by the superscript [e], exterior to this field. We have then

$$\mu^{\mathrm{l}} = \mu^{\dagger} + RT \ln \frac{n^{\mathrm{l}} RT}{V^{\mathrm{l}} P^{\dagger}} - \tfrac{1}{2}\mathbf{E}^2\left(a + \frac{\beta}{T}\right) \qquad 11.\,09.\,4$$

$$\mu^{\mathrm{e}} = \mu^{\dagger} + RT \ln \frac{n^{\mathrm{e}} RT}{V^{\mathrm{e}} P^{\dagger}} \qquad 11.\,09.\,5$$

The equilibrium distribution is determined by

$$\mu^{\mathrm{l}} = \mu^{\mathrm{e}} \qquad 11.\,09.\,6$$

Substituting (4) and (5) into (6), we obtain, writing c for n/V,

$$RT \ln \frac{c^{\mathrm{l}}}{c^{\mathrm{e}}} - \tfrac{1}{2}\mathbf{E}^2\left(a + \frac{\beta}{T}\right) = 0 \qquad 11.\,09.\,7$$

or

$$\frac{c^{\mathrm{l}}}{c^{\mathrm{e}}} = \exp\left\{\frac{\mathbf{E}^2}{2RT}\left(a + \frac{\beta}{T}\right)\right\} \qquad 11.\,09.\,8$$

Since a is always positive and β is either positive or zero, it follows that c is always greater inside the field than outside it. Thus every perfect gas is attracted into an electric field.

§ 11.\,10 RATIONALIZATION

There are two distinct and mutually contradictory conventional systems of defining electrostatic quantities. In the more modern system, called the *rational* system, the electric quantities are defined in such a manner that the factor 4π occurs frequently in formulae relating to point charges, but not in the formulae relating to parallel plate condensers. In the older *irrational* (a better word than *unrationalized*) system this situation is reversed.

As the *rational* system has not yet found wide use by physicists or chemists in Britain, we have throughout this chapter used the irrational system. Any formula in the irrational system is transformed to the rational system by replacement of $\varepsilon/4\pi$ by ε and replacement of ε_0 by $\varepsilon_0/4\pi$. The reader can verify that the name *rationalization* is justified.

MAGNETIC SYSTEMS

§ 12. 01 INTRODUCTION

In order to apply thermodynamics to magnetic systems we have merely to extend our previous formulae by including extra terms for the magnetic work. In principle the procedure is straightforward and should cause no difficulty. There is however a serious incidental difficulty, namely that of finding the correct general expression for magnetic work. We should expect to be able to discover such an expression by consulting any reputable text-book on electromagnetism. Unfortunately this is far from the case. The treatment given in most text-books is altogether inadequate. In most cases the derivations of formulae for magnetic work assume either explicitly or implicitly that the permeability of each piece of matter is a constant, whereas from a thermodynamic viewpoint one of the questions of greatest interest is how the permeability varies with the temperature. It is therefore desirable, if not essential, to start from formulae which are not restricted to the assumption that the permeability of each piece of matter is invariant. In many, if not most, text-books on electromagnetism the treatment of magnetic work suffers from other even more serious defects. In many cases the treatment is based on a discussion of permanent magnets imagined to be constructed by bringing together (reversibly ?) from infinity an infinite number of infinitesimal magnetic elements. Actually a permanent magnet is an idealization far from reality. It is true that magnets can be made which are nearly permanent with respect to changes in position, but they are never permanent with respect to changes of temperature. Increase of temperature is usually accompanied by an irreversible loss of magnetization. Whatever may be the use of the conception of a permanent magnet in the theory of such instruments as compasses, galvanometers and dynamos it is not a useful conception as a basis for the analysis of magnetic work when changes of temperature may be important. The worst text-books give formulae for magnetic work which not only are of restricted applicability, but even contain wrong signs. Fortunately there are a few

TABLE 12.1

Dimensions of Electric and Magnetic Quantities
L denotes length, T time, U energy and Q electric charge

Symbol	Name	Dimensions
Q	Electric charge	Q
i	Current	QT^{-1}
d$\mathbf{s}$	Element of length	L
id$\mathbf{s}$	Element of current	QLT^{-1}
ψ	Electrostatic potential	UQ^{-1}
$\mathbf{A}$	Magnetic vector potential	$UL^{-1}TQ^{-1}$
$\mathbf{E}$	Electric field	$UL^{-1}Q^{-1}$
$\mathbf{B}$	Magnetic induction	$UL^{-2}TQ^{-1}$
$\varepsilon_0\mathbf{E}$		QL^{-2}
$\mathbf{B}/\mu_0$		$QL^{-1}T^{-1}$
ε_0		$Q^2L^{-1}U^{-1}$
μ_0		$UQ^{-2}L^{-1}T^2$
μ_0^{-1}		$Q^2LT^{-2}U^{-1}$
$\varepsilon_0\mu_0$		$L^{-2}T^2$
$\varepsilon_0\mathbf{E}^2$		UL^{-3}
$\mathbf{B}^2/\mu_0$		UL^{-3}

1. Inasmuch as an element of current is the analogue in a magnetic system of an element of electric charge in an electrostatic system, we observe that μ_0^{-1}, not μ_0, is the analogue of ε_0.
2. $(\varepsilon_0\mu_0)^{-\frac{1}{2}}$ has the dimensions of a velocity; it is well known that this quantity is equal to the speed of propagation of electromagnetic waves in empty space.
3. The quantities $\varepsilon_0\mathbf{E}^2$ and $\mathbf{B}^2/\mu_0$ both have the dimensions of energy density or pressure.

The values of ε_0 and μ_0 and related quantities in the *rational* system are as follows: *

$$\varepsilon_0 = \frac{1}{4\pi}\frac{\text{franklin}^2}{\text{erg cm}} = 7.958 \times 10^{-2}\frac{\text{franklin}^2}{\text{erg cm}} = 8.854 \times 10^{-12}\frac{\text{C}^2}{\text{J m}}$$

$$\frac{1}{\mu_0} = \frac{10^7}{4\pi}\frac{\text{C}^2\,\text{m}}{\text{J s}^2} = 7.958 \times 10^5\frac{\text{C}^2\,\text{m}}{\text{J s}^2}$$

$$\mu_0 = \frac{4\pi}{10^7}\frac{\text{J s}^2}{\text{C}^2\,\text{m}} = 1.2566 \times 10^{-6}\frac{\text{J s}^2}{\text{C}^2\,\text{m}}$$

* The name *franklin* is used to denote a charge which repels a similar charge in vacuo at a distance one centimetre with a force of one dyne. See *Nature* 1941 **148** 751.

$$\varepsilon_0\,\mu_0 = 1.1126 \times 10^{-17}\,\mathrm{s^2\,m^{-2}}$$

$$\frac{1}{\varepsilon_0\,\mu_0} = 8.988 \times 10^{16}\,\mathrm{m^2\,s^{-2}}$$

$$\frac{1}{\sqrt{\varepsilon_0\,\mu_0}} = 2.9979 \times 10^{8}\,\mathrm{m\,s^{-1}}$$

§ 12. 05 SIMPLEST EXAMPLES OF FIELDS IN EMPTY SPACE

The formulae of the previous section are sufficient to specify completely the $\mathbf{E}$ field due to any given distribution of charges in empty space or the $\mathbf{B}$ field due to any given distribution of currents in empty space. The quantitative application of these formulae is however complicated and tedious except for the simplest systems having a high degree of symmetry. We shall consider briefly one such electrostatic system and one such magnetic system.

As the electrostatic system we choose the parallel plate condenser, already discussed in the previous chapter, neglecting edge effects. If charges Q and $-Q$ are distributed uniformly over the two plates each of area A at a distance l apart, then in the absence of any matter between the plates the electric field is uniform, normal to the plates and has the value

$$\mathbf{E} = \frac{Q}{\varepsilon_0 A} \qquad\qquad 12.\,05.\,1$$

This formula differs from formula (11. 02. 1) by a factor 4π because the latter is expressed in the *irrational* system.

As an example of a magnetic system having simple symmetry we choose a long uniform solenoid and we ignore end effects. The magnetic induction inside the empty solenoid is then uniform, parallel to the axis and has the value

$$\mathbf{B} = \frac{\mu_0\,i}{l} \qquad\qquad 12.\,05.\,2$$

when the intensity of the current is i and there is one turn per length l.

For reasons which will appear later it is instructive to rewrite (1) and (2) in somewhat different forms. We rewrite (1) as

$$\varepsilon_0\mathbf{E} \quad \frac{Ql}{V_c} \qquad\qquad 12.\,05.\,3$$

where l is the distance between the plates and $V_c = lA$ is the volume included between the plates of the condenser. The product Ql of the charge on a plate and the distance between the plates may be called the *electric moment* of the charged condenser. Thus according to (3) we observe that in this system with simple symmetry $\varepsilon_0 \mathbf{E}$ is equal to the *electric moment per unit volume*.

We likewise rewrite (2) in the form

$$\frac{\mathbf{B}}{\mu_0} = \frac{niA}{V_s} \qquad 12.\ 05.\ 4$$

where n denotes the total number of turns, A denotes the cross-section of the solenoid and $V_s = nlA$ denotes the volume contained by the solenoid. We may regard the solenoid as an *electromagnet* and we call the product niA its *magnetic moment*. We see then according to (4) that $\mathbf{B}/\mu_0$ is equal to the *magnetic moment per unit volume* of the solenoid.

From these relations we again perceive that μ_0^{-1}, not μ_0, is the analogue of ε_0.

§ 12. 06 PRESENCE OF MATTER

We shall now discuss briefly the effect of filling the parallel plate condenser and the solenoid respectively with uniform matter.

When the space between the plates of the condenser is filled with uniform matter, this matter becomes electrically polarized as a result of the field due to the charges on the plates. The *electric polarization* $\mathbf{P}$ is defined as the electric moment per unit volume induced in the matter. Owing to the symmetry of the system under consideration $\mathbf{P}$ is in this case uniform and normal to the plates. It is not difficult to see what will be the resultant effect on the field $\mathbf{E}$. We interpreted formula (12. 05. 3) to mean that $\varepsilon_0 \mathbf{E}$ is equal to the *electric moment per unit volume* of the charged condenser. It is evident that $\varepsilon_0 \mathbf{E}$ will now be equal to the resultant electric moment per unit volume due partly to the charges $\pm Q$ on the plates and partly to the polarization of the matter between the plates. Thus in place of (12. 05. 3) we shall have

$$\varepsilon_0 \mathbf{E} = \frac{Ql}{V_c} - \mathbf{P} \qquad 12.\ 06.\ 1$$

or

$$\varepsilon_0 \mathbf{E} + \mathbf{P} = \frac{Ql}{V_c} = \frac{Q}{A} \qquad 12.\ 06.\ 2$$

Thus $\varepsilon_0 \mathbf{E} + \mathbf{P}$ is now related to the charge on the condenser plates in precisely the same manner as $\varepsilon_0 \mathbf{E}$ was related to it when the condenser was empty. In other systems having lower symmetry the situation is less simple because $\mathbf{E}$ and $\mathbf{P}$ vary from place to place. The composite vector $\varepsilon_0 \mathbf{E} + \mathbf{P}$ still however plays an important role. It is called by the curious name *electric displacement* and is denoted by $\mathbf{D}$. Thus

$$\mathbf{D} \equiv \varepsilon_0 \mathbf{E} + \mathbf{P} \qquad\qquad 12.\,06.\,3$$

From the identity (3) it is evident that any two of the vectors $\mathbf{E}$, $\mathbf{P}$, $\mathbf{D}$ completely determines the remaining one. It is however a fundamental assumption of electrostatics, borne out by experiment, that at any point in a piece of matter of given composition, given temperature and given pressure any one of the vectors $\mathbf{E}$, $\mathbf{P}$, $\mathbf{D}$ completely determines the other two. If moreover the matter is isotropic, then $\mathbf{E}$, $\mathbf{P}$ and $\mathbf{D}$ have the same direction. If then we write

$$\mathbf{D} \equiv \varepsilon \mathbf{E} \qquad\qquad 12.\,06.\,4$$

the coefficient ε is a scalar quantity, provided the matter is isotropic. (Otherwise ε would be a tensor of rank two.)

The quantity ε defined by (4) is called the *permittivity* of the matter. Its value in general depends on the composition of the matter, the temperature, the pressure and the field strength. The ratio

$$\frac{\mathbf{D}}{\varepsilon_0 \mathbf{E}} - \frac{\varepsilon}{\varepsilon_0} \qquad\qquad 12.\,06.\,5$$

is called the *relative permittivity* or *dielectric coefficient* or, when its value is independent of $\mathbf{E}$, the *dielectric constant*.

It is evident from (3) that $\mathbf{P}$ and $\mathbf{D}$ have the same dimensions as $\varepsilon_0 \mathbf{E}$, namely that of charge/area. It is likewise evident from (3) and (4) that ε has the same dimensions as ε_0, so that the *dielectric coefficient* $\varepsilon/\varepsilon_0$ is a dimensionless number.

Much of the above is repetition from the previous chapter, is moreover well known and is seemingly irrelevant to magnetic systems. It is however convenient to have these relations before us for comparison with analogous but less understood magnetic relations.

We turn now to consider the effect of filling the uniform solenoid with uniform matter. As a result of the current in the solenoid the matter will behave as if it contained induced microscopic molecular current circuits or elementary magnets. According to (12. 05. 4) their

contribution to $\mathbf{B}/\mu_0$ will be equal to the magnetic moment per unit volume; this quantity is called the *magnetization* and is denoted by $\mathbf{M}$. Owing to the symmetry of the solenoid, $\mathbf{M}$ will be parallel to the axis and so (12. 05. 4) has to be replaced by

$$\frac{\mathbf{B}}{\mu_0} = \frac{niA}{V_s} + \mathbf{M} \qquad \text{12. 06. 6}$$

or

$$\frac{\mathbf{B}}{\mu_0} - \mathbf{M} = \frac{niA}{V_s} = \frac{i}{l} \qquad \text{12. 06. 7}$$

Thus the composite vector $(\mathbf{B}/\mu_0)$—$\mathbf{M}$ is now related to the current through the solenoid in precisely the same manner as $\mathbf{B}/\mu_0$ was related to it when the inside of the solenoid was empty. In other systems having lower symmetry the situation is less simple because $\mathbf{B}$ and $\mathbf{M}$ vary from place to place. The composite vector $(\mathbf{B}/\mu_0)$—$\mathbf{M}$ still however plays an important role. It is called by the misleading name * *magnetic field intensity* and is denoted by $\mathbf{H}$. Thus

$$\mathbf{H} \equiv \frac{\mathbf{B}}{\mu_0} - \mathbf{M} \qquad \text{12. 06. 8}$$

From the identity (8) it is evident that any two of the vectors $\mathbf{B}$, $\mathbf{M}$, $\mathbf{H}$ completely determine the remaining one. It is however a fundamental assumption of electromagnetic theory that at any point in a piece of matter of given composition, given temperature and given pressure any one of the vectors $\mathbf{B}$, $\mathbf{M}$, $\mathbf{H}$ completely determines the other two. This assumption is often, though not always, borne out by experiment. The phenomenon known as *hysteresis* contradicts the assumption; such phenomena are here expressly excluded from consideration. With this proviso we write

$$\mathbf{H} = \frac{\mathbf{B}}{\mu} \qquad \text{12. 06. 9}$$

and the coefficient μ is called the *permeability* of the matter. Provided the matter is isotropic μ is a scalar. (Otherwise μ would be a tensor of

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* In S , E. T. p. 12 $\mathbf{E}$ and $\mathbf{B}$ are called *force vectors* while $\mathbf{D}$ and $\mathbf{H}$ are called *derived vectors*. Confusion of thought would be diminished if the following names were used:

$\mathbf{E}$ electric force vector;	$\mathbf{B}$ magnetic force vector.
$\mathbf{D}$ electric derived vector;	$\mathbf{H}$ magnetic derived vector.

rank two.) The value of μ in general depends on the composition, the temperature, the pressure and the field strength. The ratio μ/μ_0 will be referred to as the *relative permeability* of the substance, or when its value is independent of **B** as the *magnetic constant*.

§ 12.07 ELECTRIC AND MAGNETIC WORK

Having completed our elementary review of the physical significance of the vectors **E**, **D** and **B**, **H** we shall quote without proof general formulae for electric and magnetic work. A brief outline of the derivation of these formulae from Maxwell's equations is given in appendix A at the end of this chapter.

We first consider an electrostatic system consisting of charged conductors and dielectrics. For any infinitesimal change in the system, produced by moving either an electric charge or a conductor or a dielectric, the electric work w done on the system is given by *

$$ w = \int dV\, \mathbf{E}\, d\mathbf{D} \qquad 12.07.1 $$

where $d\mathbf{D}$ denotes the increment of **D** in the element of volume dV and the integration extends over all space, or that part of space where the electric field does not vanish.

In the simplest case of a parallel plate condenser containing a uniform dielectric, if we neglect edge effects, **E** and **D** vanish outside the condenser, while between the plates they are uniform having the values

$$ \mathbf{D} \quad \frac{Q}{A} \qquad 12.07.2 $$

$$ \mathbf{E} \quad \frac{Q}{\varepsilon A} \qquad 12.07.3 $$

where $\pm Q$ denotes the charge on either plate of area A. If then l denotes the distance between the plates and V_c the volume contained between them, formula (1) reduces to

$$ w = V_c \frac{\varkappa}{\varepsilon A} \frac{dQ}{A} $$

$$ = \frac{l}{A} \frac{Q\, dQ}{\varepsilon} \qquad 12.07.4 $$

in agreement with formula (11.04.2) apart from the disappearance of a factor 4π owing to rationalization.

* See, S., E. T. p. 108.

We turn now to a magnetic system consisting of current circuits and magnetic matter, concerning which our only restrictive assumption is the absence of hysteresis. For any infinitesimal change in the system either by changing the current in any circuit or by moving any conductor carrying a current, the magnetic work done on the system is [*]

$$w = \int dV \, \mathbf{H} \, d\mathbf{B} \qquad\qquad 12.\,07.\,5$$

where $d\mathbf{B}$ is the increment of $\mathbf{B}$ in the element of volume dV and the integration extends over all space, or that part of space where the magnetic field does not vanish.

Since we have been at pains to emphasize that $\mathbf{B}$ is the analogue of the force vector $\mathbf{E}$, while $\mathbf{H}$ is the analogue of the derived vector $\mathbf{D}$, the reader may justifiably express surprise that formula (5) contains as integrand $\mathbf{H}d\mathbf{B}$, not $\mathbf{B}d\mathbf{H}$. The explanation of this paradox is that the analogy must not be pushed too far, because, whereas the electrostatic energy due to fixed charges is potential energy, the magnetic energy due to electric currents is kinetic energy [†].

In the simplest case of a long solenoid filled with a uniform isotropic substance, if we neglect end effects, $\mathbf{B}$ and $\mathbf{H}$ vanish outside the solenoid, while inside they are uniform having the values

$$\mathbf{H} = \frac{i}{l} \qquad\qquad 12.\,07.\,6$$

$$\mathbf{B} = \frac{\mu i}{l} \qquad\qquad 12.\,07.\,7$$

where i denotes the current and l the length per turn. If then $V_{\mathbf{s}}$ denotes the internal volume of the solenoid. L its length, A its cross-section and n the total number of turns, formula (5) becomes

$$w = V_{\mathbf{s}} \frac{i}{l} \frac{d(\mu i)}{l}$$

$$= \frac{A}{L} n^2 i \, d(\mu i) \qquad\qquad 12.\,07.\,8$$

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[*] See Appendix A at end of chapter.

[†] While the Hamiltonians contain as integrands $\mathbf{E}d\mathbf{D}$ and $\mathbf{H}d\mathbf{B}$, the Lagrangians contain as integrands — $\mathbf{E}d\mathbf{D}$ and $\mathbf{B}d\mathbf{H}$.
See Guggenheim. *Proc. Roy. Soc.* A 1936 **155** 63.
Broer, *Physica* 1946 **12** 49.

§ 12. 08 FORMULA FOR FREE ENERGY

Once we know the general formula for magnetic work it is, as already mentioned in § 12. 01, a straightforward matter to write down thermodynamic formulae of general validity. For the sake of brevity and simplicity we shall confine our discussion to phases of constant volume. The formulae may still be applied to solid and liquid phases at constant pressure as an approximation equivalent to neglect of thermal expansion, compressibility and *magnetostriction*, the name for volume changes due to change of the magnetic induction.

Consider now a system consisting of linear conductors and magnetic matter and suppose the currents gradually increased from zero to final values corresponding to final values of **B** and **H** at each point of the system. Then the magnetic work w done on the system when the field is thus built up is

$$w = \int dV \int_0^{\mathbf{B}} \mathbf{H} \, d\mathbf{B} \qquad \text{12. 08. 1}$$

where the first integration extends over all space. The second integral will depend on the relation between **B** and **H** which in turn depends on the temperature at each stage. Let us now specify that the path of integration shall be isothermal. Then the work w is equal to the increase in the free energy F of the system. We accordingly have

$$F = F^0 + \int dV \int_0^{\mathbf{B}} \mathbf{H} \, d\mathbf{B} \qquad \text{12. 08. 2}$$
$$\text{\small (}T\text{ const.)}$$

where F^0 denotes the free energy when **B** is everywhere zero, that of volume is to say when no currents are flowing.

In the simplest case of a uniform field, as when a long solenoid of volume V is filled with a uniform substance, (2) can be written as

$$F - F^0 = \int_0^{\mathbf{B}} \mathbf{H} \, d\mathbf{B}$$
$$\text{\small (}T\text{ const.)}$$
$$\int_0^{\mathbf{B}} \frac{\mathbf{B}}{\mu} \, d\mathbf{B} \qquad \text{12. 08. 3}$$
$$\text{\small (}T\text{ const.)}$$

§ 12. 09 OTHER THERMODYNAMIC FUNCTIONS

From the formula for the free energy F we can immediately derive formulae for the entropy S and the total energy U by differentiation

with respect to T. For the sake of brevity and simplicity we shall confine ourselves to the formulae valid in a region where composition and field are uniform. Using the superscript ^{0} to denote values of a function when **B** is zero, we derive from (12. 08. 3)

$$\frac{S^0}{V} = -\frac{\partial}{\partial T}\int_0^{\mathbf{B}}\frac{\mathbf{B}}{\mu}\,d\mathbf{B}$$
$$\text{\small(T const.)}$$

$$= -\int_0^{\mathbf{B}}\frac{\partial\,(1/\mu)}{\partial T}\,\mathbf{B}\,d\mathbf{B} \qquad 12.\ 09.\ 1$$
$$\text{\small(T const.)}$$

$$\frac{U - U_0}{V} = \int_0^{\mathbf{B}}\left\{\frac{1}{\mu} - T\,\frac{\partial\,(1/\mu)}{\partial T}\right\}\mathbf{B}\,d\mathbf{B} \qquad 12.\ 09.\ 2$$
$$\text{\small(T const.)}$$

§ 12. 10 CASE OF LINEAR INDUCTION

Hitherto we have imposed no restriction on the relation between **H** and **B**. The permeability μ was defined by

$$\mu \equiv \frac{\mathbf{B}}{\mathbf{H}} \qquad 12.\ 10.\ 1$$

and in general μ depends on **B** (or **H**) as well as on the temperature. For most materials, other than those exhibiting hysteresis, at the field strengths ordinarily used in the laboratory and at ordinary temperatures, it is found that μ is, at a given temperature, independent of **B**. Under these conditions the integrations in the formulae of the previous two sections can be performed explicitly. Thus formulae (12. 08. 3), (12. 09. 1) and (12. 09. 2) reduce respectively to

$$\frac{F - F^0}{V} = \frac{1}{\mu}\,\tfrac{1}{2}\mathbf{B}^2 = \tfrac{1}{2}\mathbf{H}\mathbf{B} = \tfrac{1}{2}\mu\mathbf{H}^2 \qquad 12.\ 10.\ 1$$

$$\frac{S - S^0}{V} = \frac{1}{\mu^2}\frac{d\mu}{dT}\,\tfrac{1}{2}\mathbf{B}^2 = \frac{d\mu}{dT}\,\tfrac{1}{2}\mathbf{H}^2 \qquad 12.\ 10.\ 2$$

$$\frac{U - U^0}{V} = \left(\mu + T\frac{d\mu}{dT}\right)\tfrac{1}{2}\mathbf{H}^2 \qquad 12.\ 10.\ 3$$

Although a variation of μ with **B** at constant temperature is the exception, it does occur especially at low temperatures. In particular this phenomenon of *magnetic saturation* has been observed for hydrated

gadolinium sulphate *. The formulae of the present section are then not applicable.

§ 12. 11 SPHERICAL SPECIMEN IN UNIFORM FIELD

The relations developed so far involve integration over all space or that part of space where the field does not vanish. These integrations are usually too complicated to be practicable except in the case of a long solenoid completely filled with a uniform material. Unfortunately this example is of little practical interest. The experimenter is more interested in the behaviour of a specimen of matter introduced into a magnetic field, which was uniform before the introduction of the specimen. We shall begin by considering as the simplest case, a spherical specimen.

Consider a uniform magnetic field such as that inside a long empty solenoid and denote the force vector (induction) by $\mathbf{B_e}$. Suppose now that a sphere of radius a consisting of uniform isotropic material is introduced into this field. It is well known that the resultant magnetization $\mathbf{M}$ in the sphere is uniform and parallel to $\mathbf{B_e}$. If then we denote the total magnetic moment of the sphere by $\mathbf{m}$, we have

$$\mathbf{m} = \frac{4\pi}{3} a^3 \mathbf{M} \qquad 12.\,11.\,1$$

If now $\mathbf{B_e}$ is varied, there is a consequent variation of $\mathbf{M}$ and $\mathbf{m}$. The work done on the specimen by the external field is then

$$w = \mathbf{B_e}\,d\mathbf{m}$$

$$= \frac{4\pi}{3} a^3 \mathbf{B_e}\,d\mathbf{M} \qquad 12.\,11.\,2$$

To most readers this formula will be well known. It is however far from obvious that it is equivalent to or derivable from formula (12. 07. 5). As a matter of fact (2) can be derived from the more general relation (12. 07. 5). The proof is given † in appendix C at the end of this chapter.

It is important to remember that the value of $\mathbf{B}$ inside the spherical

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* Woltjer and Onnes, *Comm. Phys. Lab. Leiden* 1923 no. 167c.

† The author knows of no text-book which contains this proof. There are indeed to be found proofs valid only under the special condition of a linear relation between $\mathbf{M}$ and $\mathbf{B_e}$.

specimen, though uniform, is not equal to $\mathbf{B_e}$. In fact inside the specimen

$$\mathbf{B} = \mathbf{B_e} + \tfrac{2}{3}\mu_0\mathbf{M}$$ 12. 11. 3

For the free energy F we deduce immediately from (2)

$$\mathrm{d}F = \frac{4\pi}{3}\,a^3\mathbf{B_e}\,\mathrm{d}\mathbf{M} \quad \text{(const. } T)$$ 12. 11. 4

If now we denote by F^1 the energy of interaction between the specimen and the field, we have

$$\frac{F^1}{V} = \int_0^{\mathbf{M}} \mathbf{B_e}\,\mathrm{d}\mathbf{M}$$
$$\text{(\textit{T} const.)}$$ 12. 11. 5

where V denotes the volume of the specimen.

It is clear from (4) that the free energy F is the characteristic function for the variables T, $\mathbf{M}$. For most purposes a more useful function is the characteristic function for the variables T, $\mathbf{B_e}$ denoted by $\mathcal{J}$ and defined by

$$\mathcal{J} = F - \mathbf{B_e}\mathbf{m}$$ 12. 11. 6

The contribution $\mathcal{J}^1$ to $\mathcal{J}$ from the interaction between the specimen and the field is given by

$$\frac{\mathcal{J}^1}{V} = -\int_0^{\mathbf{B_e}} \mathbf{M}\,\mathrm{d}\mathbf{B_e}$$
$$\text{(\textit{T} const.)}$$ 12. 11. 7

For the entropy of interaction S^1 between the specimen and the field we derive from (7)

$$\frac{S^1}{V} = \int_0^{\mathbf{B_e}} \left(\frac{\partial \mathbf{M}}{\partial T}\right)_{\mathbf{B_e}}\,\mathrm{d}\mathbf{B_e}$$
$$\text{(\textit{T} const.)}$$ 12. 11. 8

These formulae are independent of the form of the functional relation between $\mathbf{M}$ and $\mathbf{B_e}$. In the particular case of linear induction described in § 12. 10 $\mathbf{B}/\mathbf{H}$ and $\mathbf{M}/\mathbf{B}$ are at a given temperature constant. It

follows from (3) that M/B_e is constant at each temperature. We can then perform the integrations, obtaining

$$\frac{F^1}{V} = \tfrac{1}{2}MB_e \qquad\qquad 12.\,11.\,9$$

$$\frac{H^1}{V} = -\tfrac{1}{2}MB_e \qquad\qquad 12.\,11.\,10$$

$$\frac{S^1}{V} = \tfrac{1}{2}\frac{\partial M}{\partial T}B_e \qquad\qquad 12.\,11.\,11$$

The limitations on formulae (9), (10) and (11) are the same as on the formulae of § 12.10.

§ 12.12 SPECIMENS WITH OTHER SHAPES

If the specimen introduced into the uniform external field B_e instead of being spherical, is a spheroid with its axis of symmetry parallel to B_e then the resultant magnetization M is still parallel to B_e. The total magnetic moment m of the specimen is equal to the product of M and the volume of the spheroid. If the semi-axes of the spheroid are of length a, b, b then

$$m = \frac{4\pi}{3}ab^2M \qquad\qquad 12.\,12.\,1$$

When the field B_e is varied the work w done by the field on the specimen is, as proved in appendix C at the end of this chapter, given by

$$w = \int dV\; B_e\, dM$$

$$= \frac{4\pi}{3}ab^2 B_e\, dM \qquad\qquad 12.\,12.\,2$$

For the thermodynamic functions F^1, H^1 and S^1, formulae (12.11.5), (12.11.7) and (12.11.8) are still valid. In the particular case of linear induction formulae (12.11.9), (12.11.10) and (12.11.11) are valid.

The relation between B inside the specimen and B_e is still linear, of the form

$$B = B_e + a\mu_0 M \qquad\qquad 12.\,12.\,3$$

where a is a positive fractional coefficient depending on the ratio a/b. The derived vector H is then given by

$$H = \frac{B}{\mu_0} - M = \frac{B_e}{\mu_0} - (1-a)\,M \qquad\qquad 12.\,12.\,4$$

The numerical coefficient $(1 — a)$ in (4) has in the past been given the curious name *demagnetizing coefficient*, but the name has nothing to recommend it.

If the specimen is an ellipsoid having three unequal principal axes, the conditions are slightly more complicated. If the specimen is not an ellipsoid, then the induced magnetization is not uniform and so the situation is considerably more complicated.

§ 12. 13 DIAMAGNETIC, PARAMAGNETIC AND FERROMAGNETIC SUBSTANCES

Substances are divided into three classes according to their magnetic properties. These have the names *diamagnetic, paramagnetic* and *ferromagnetic*.

In a *diamagnetic* substance μ has a constant value less than μ_0, independent of the field strength and of the temperature. For such a substance there is no magnetic term in the entropy and consequently there is no distinction between total energy and free energy. Thus the thermodynamics of diamagnetic substances is so simple as to be trivial.

In a *paramagnetic* substance μ has a value greater than μ_0 and varying with the temperature. The value of μ also depends on the field, but usually varies but little with the field except in high fields or at low temperatures. Paramagnetic substances form the class to which the application of thermodynamics is most interesting and useful. The remaining sections of this chapter will be devoted almost entirely to paramagnetic substances.

A characteristic of *ferromagnetic* substances is the occurrence of *hysteresis*. This means that **M** is not a single valued function of the field. When the field is varied the changes in magnetization are usually not reversible. The application of thermodynamics is accordingly difficult. Such attempts as have been made to apply thermodynamics to ferromagnetic substances are still controversial and nothing further will be said of them. Our only remarks concerning ferromagnetic substances will be of a general qualitative nature.

In ferromagnetic substances μ is greater than μ_0 and usually considerably greater than in paramagnetic substances. There can even be magnetization in the absence of any external field. This is called *permanent magnetization* or *remanent magnetization*.

When the temperature of a ferromagnetic substance is raised, the substance eventually becomes paramagnetic. The temperature at

which this change occurs is called the *Curie temperature*. The change is a transition of higher order as defined in chapter 7. Thus the Curie temperature is a lambda point, in fact the first example of a lambda point to be discovered.

§ 12. 14 SIMPLE PARAMAGNETIC BEHAVIOUR

We shall describe in some detail the behaviour of those paramagnetic substances whose magnetic properties are entirely due to electron spin. The behaviour of the larger class whose magnetic properties are due partly or entirely, to orbital angular momentum is qualitatively similar but quantitatively more complicated. A description of these will not be attempted here as it would require too much space. The reader interested will have to turn to a more specialized source of information.[*]

The fundamental unit of magnetic moment in electron theory is *Bohr's magneton* and all magnetic moments will be expressed in terms of this unit. Bohr's magneton is denoted by β and is defined by

$$\beta = \frac{e}{m_e} \frac{h}{4\pi} \qquad \qquad 12.\,14.\,1$$

where $-e$ denotes the charge and m_e the mass of an electron while h, as usual, denotes Planck's constant. If we multiply (1) by Avogadro's number L, we obtain the corresponding molar unit

$$L\beta = \frac{Le}{m_e} \frac{h}{4\pi} = \frac{Fh}{4\pi m_e} \qquad \qquad 12.\,14.\,2$$

where F denotes the faraday. Inserting the numerical values

$$F = 9.650 \times 10^4 \, \text{C mole}^{-1}$$
$$m_e = 9.108 \times 10^{-28} \, \text{g}$$
$$h = 6.625 \times 10^{-27} \, \text{g cm}^2 \, \text{s}^{-1}$$

we obtain

$$L\beta = \frac{9.650 \times 10^4 \times 6.625 \times 10^{-27}}{4\pi \times 9.108 \times 10^{-28}} \, \text{C cm}^2 \, \text{s}^{-1} \, \text{mole}^{-1}$$
$$= 5.586 \times 10^4 \, \text{A cm}^2 \, \text{mole}^{-1}$$
$$= 5.586 \, \text{A m}^2 \, \text{mole}^{-1} \qquad \qquad 12.\,14.\,3$$

Correspondingly for β we have

$$\beta = 5.586 \times 1.6601 \times 10^{-24} \, \text{A m}^2$$
$$= 9.273 \times 10^{-24} \, \text{A m}^2 \qquad \qquad 12.\,14.\,4$$

[*] Van Vleck, *Electric and Magnetic Susceptibilities* 1932 p. 259.

Following standard spectroscopic notation we shall denote the resultant spin quantum number by S, so that the multiplicity is $2S + 1$. Examples of values of S for some typical paramagnetic ions of transition elements are given in table 12. 2. The first and last ions in the table, having $S = 0$, are diamagnetic.

TABLE 12. 2

Multiplicities of typical paramagnetic ions of transition elements

Ions	Number of $3d$ electrons	S	$2S + 1$
Sc^{3+}	0	0	1
Sc^{2+}, Ti^{3+}, V^{4+}	1	$\frac{1}{2}$	2
Ti^{2+}, V^{3+}	2	1	3
V^{2+}, Cr^{3+}	3	$1\frac{1}{2}$	4
Cr^{2+}, Mn^{3+}	4	2	5
Mn^{2+}, Fe^{3+}	5	$2\frac{1}{2}$	6
Fe^{2+}	6	2	5
Co^{2+}	7	$1\frac{1}{2}$	4
Ni^{2+}	8	1	3
Cu^{2+}	9	$\frac{1}{2}$	2
Cu^+, Zn^{2+}	10	0	1

We now consider a substance such as ferric alum $NH_4Fe(SO_4)_2 . 12H_2O$ each molecule of which contains a considerable number of atoms, in this example 52, only one of which, in this case Fe, is paramagnetic. In such a substance the paramagnetic ions, in this case Fe^{3+}, may usually be considered as mutually independent, each making its own contribution to the paramagnetism of the substance. We shall denote the molar volume as usual by V_m, this being the volume which contains L paramagnetic ions.

We consider a small spherical specimen of such a substance placed in a uniform external magnetic field with induction $\mathbf{B_e}$. Then for the independent variables T, $\mathbf{B_e}$ the characteristic function $\mathcal{J}^1$ of the interaction between the specimen and the field is given by *

$$\mathcal{J}^1 \frac{V_m}{V} = - RT \ln \frac{\sinh \{(2S + 1) L\beta \mathbf{B_e}/RT\}}{\sinh \{L\beta \mathbf{B_e}/RT\}} \qquad 12. 14. 5$$

where V denotes the volume of the specimen. Formula (5) is essentially due to Brillouin.

* See Van Vleck, *Electric and Magnetic Susceptibilities* 1932. Stoner, *Magnetism and Matter* 1934.

From formula (5) we can derive all the thermodynamic formulae relating to the magnetic properties of the specimen. The magnetic moment **m** of the specimen is determined by

$$\mathbf{m} = \cdot\frac{\partial \mathcal{J}^1}{\partial \mathbf{B_e}} \qquad 12.\,14.\,6$$

and the magnetization **M** by

$$\mathbf{M} = -\frac{1}{V}\frac{\partial \mathcal{J}^1}{\partial \mathbf{B_e}} \qquad 12.\,14.\,7$$

From (5) and (7) we derive

$$\mathbf{M}V_m = (2S+1)\,L\beta\,\coth\{(2S+1)\,L\beta\mathbf{B_e}/RT\}$$
$$- L\beta\,\coth\{L\beta\mathbf{B_e}/RT\} \qquad 12.\,14.\,8$$

We shall study the particular case $S = \frac{1}{2}$ before continuing with the general case. When $S = \frac{1}{2}$, formula (8) reduces to the simple form

$$\mathbf{M}V_m = L\beta\,\tanh\{L\beta\mathbf{B_e}/RT\} \qquad 12.\,14.\,9$$

We see at once that for sufficiently small field strengths we may replace (9) by the approximation

$$\mathbf{M}V_m = \frac{(L\beta)^2}{RT}\,\mathbf{B_e} \qquad (L\beta\mathbf{B_e} \ll RT) \qquad 12.\,14.\,10$$

so that **M** is directly proportional to $\mathbf{B_e}$ and inversely proportional to T. This behaviour is known as *Curie's law*. At the opposite extreme of sufficiently high values of $\mathbf{B_e}$ we may replace (9) by the approximation

$$\mathbf{M}V_m = L\beta \qquad (L\beta\mathbf{B_e} \gg RT) \qquad 12.\,14.\,11$$

so that **M** is independent of $\mathbf{B_e}$ and of T. This behaviour is called *magnetic saturation*.

We shall soon see for all values of S that Curie's law is valid in sufficiently low fields and that saturation occurs in sufficiently high fields.

We now return to the general formula (5) and consider its simplification in the two extremes of large and of small $\mathbf{B_e}$. Considering first large values of $\mathbf{B_e}$ we replace each sinh by $\frac{1}{2}$ exp and obtain immediately

$$\mathcal{J}^1\frac{V_m}{V} = -2SL\beta\mathbf{B_e} \qquad (L\beta\mathbf{B_e} \gg RT) \qquad 12.\,14.\,12$$

From (7) and (12) we derive

$$\mathbf{M}V_m = 2SL\boldsymbol{\beta} \qquad (L\boldsymbol{\beta}\mathbf{B}_e \gg RT) \qquad 12.14.13$$

representing saturation.

We turn now to the opposite extreme of small $\mathbf{B}_e$. We expand each sinh as a power series retaining the first two terms. We then expand the logarithm, again retaining the first two terms. We thus obtain

$$\mathcal{J}^1 \frac{V_m}{V} = -RT \ln(2S+1) - \frac{4S(S+1)}{6} \frac{(L\boldsymbol{\beta}\mathbf{B}_e)^2}{RT}$$

$$(L\boldsymbol{\beta}\mathbf{B}_e \ll RT) \qquad 12.14.14$$

From (7) and (14) we derive

$$\mathbf{M}V_m = \frac{4S(S+1)(L\boldsymbol{\beta})^2}{3RT} \mathbf{B}_e \qquad (L\boldsymbol{\beta}\mathbf{B}_e \ll RT) \qquad 12.14.15$$

so that $\mathbf{M}$ is directly proportional to $\mathbf{B}_e$ and inversely proportional to T in accordance with Curie's law.

Formula (15) has been verified experimentally for numerous substances. The more general theoretical relation (8) between $\mathbf{M}$ and $\mathbf{B}_e$ extending from the extreme of Curie's law to the opposite extreme of saturation has been quantitatively verified [*] for hydrated gadolinium sulphate, in which the paramagnetic Gd^{3+} ion is in an ^8S state with $S = 3\frac{1}{2}$.

§ 12.15 ENTROPY OF SIMPLE PARAMAGNETIC SUBSTANCES

We continue to restrict our discussion to substances whose paramagnetism is due entirely to electron spin. The behaviour of other paramagnetic substances is qualitatively similar but more complicated.

By differentiating (12.14.5) with respect to T we can obtain a general formula for S^1 the entropy of interaction between the field and the specimen. For the sake of brevity we shall however confine ourselves to the two extreme cases of $\mathbf{B}_e$ large and of $\mathbf{B}_e$ small.

At magnetic saturation according to (12.14.12) the function $\mathcal{J}^1$ is independent of the temperature and the entropy S^1 vanishes.

Under the opposite conditions of small field we derive from (12.14.14)

$$\frac{S^1}{R} \frac{V_m}{V} = \ln(2S+1) - \frac{4S(S+1)}{6} \left(\frac{L\boldsymbol{\beta}\mathbf{B}_e}{RT}\right)^2 \qquad (L\boldsymbol{\beta}\mathbf{B}_e \ll RT)$$

$$12.15.1$$

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[*] Woltjer and Onnes, *Comm Phys. Lab Leiden* 1923 no. 167c.

§ 12. 16 ADIABATIC DEMAGNETIZATION

In a system whose state can be completely defined by the temperature T and the external magnetic field $\mathbf{B}_e$ (all other degrees of freedom such as pressure and composition being either irrelevant or held constant), the equation for a reversible adiabatic process is

$$S(T, \mathbf{B}_e) = \text{const.} \qquad \text{(adiabatic)} \qquad 12.\,16.\,1$$

In a sample of a paramagnetic substance, such as ferric alum, in the temperature range 2 °K to 4 °K all contributions to the entropy from translational, rotational, intramolecular, and vibrational degrees of freedom are effectively zero, while any contributions from intranuclear degrees of freedom remain constant. Hence for adiabatic variations of the field $\mathbf{B}_e$, we have

$$S^1(T, \mathbf{B}_e) = \text{const.} \qquad \text{(adiabatic)} \qquad 12.\,16.\,2$$

Provided $\mathbf{B}_e$ is not too great, we may use formula (12. 15. 1) for S^1, so that (2) leads to

$$\frac{\mathbf{B}_e}{T} = \text{const.} \qquad \text{(adiabatic)} \qquad 12.\,16.\,3$$

Thus when the field is reduced the temperature drops proportionally. This is the principle of cooling by adiabatic demagnetization.

§ 12. 17 UNATTAINABILITY OF ABSOLUTE ZERO

By means of adiabatic demagnetization temperatures as low as 10^{-3} °K have been reached. It would appear from formula (12. 16. 3) that by reducing the external field to zero, one should reach $T = 0$ in contradiction of Nernst's theorem. The resolution of this paradox is that before $T = 0$ is reached, usually in the region $T \simeq 10^{-2}$ °K, the formulae of § 12. 14 and § 12. 15 cease to be applicable. In other words, at some such temperature the substance ceases to be paramagnetic, but becomes eventually either diamagnetic or ferromagnetic.

In the change from the paramagnetic to the diamagnetic or ferromagnetic state, the molar entropy in zero magnetic field is altogether reduced by an amount

$$R \ln(2S + 1) \qquad 12.\,17.\,1$$

Hence by comparison with (12. 15. 1), we see that the value of S^1 for zero field falls to zero. This is in agreement with the third principle of thermodynamics as expounded in chapter 4. The reader must turn elsewhere * for details of such changes.

* For example Debye, *Ann. Phys., Lpz.* 1938 **32** 85.

An excellent elementary account is given by Simon, *Very Low Temperatures,* Science Museum Handbook 1937 No. 3 p. 58.

DERIVATION* OF FORMULAE FOR ELECTROSTATIC AND MAGNETIC WORK

We start from Maxwell's equations in their rational form, namely

$$\text{curl } \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} = 0 \qquad\qquad 12\text{A. } 1$$

$$\text{curl } \mathbf{H} - \frac{\partial \mathbf{D}}{\partial t} = \mathbf{J} \qquad\qquad 12\text{A. } 2$$

where $\mathbf{J}$ denotes current density, while $\mathbf{E}$, $\mathbf{B}$, $\mathbf{D}$, $\mathbf{H}$ have their usual meanings.

We multiply (2) by $\mathbf{E}$, (1) by $\mathbf{H}$ and subtract. Using the identity

$$\mathbf{H} \text{ curl } \mathbf{E} - \mathbf{E} \text{ curl } \mathbf{H} = \text{div } (\mathbf{E} \times \mathbf{H}) \qquad\qquad 12\text{A. } 3$$

we obtain

$$\text{div } (\mathbf{E} \times \mathbf{H}) + \mathbf{E}\mathbf{J} + \mathbf{E} \frac{\partial \mathbf{D}}{\partial t} + \mathbf{H} \frac{\partial \mathbf{B}}{\partial t} = 0 \qquad\qquad 12\text{A. } 4$$

We now multiply (4) by $dVdt$ and integrate over the whole volume of the system. Assuming that the field vanishes at the boundary of the system we obtain

$$\int dV \, \mathbf{E}\mathbf{J} \, dt + \int dV \, \mathbf{E} \, d\mathbf{D} + \int dV \, \mathbf{H} \, d\mathbf{B} = 0 \qquad\qquad 12\text{A. } 5$$

Now consider a cylindrical volume element parallel to the current density of length dl and of cross-section dA. Then, according to the definition of current density $\mathbf{J}$, the quantity of electricity flowing through this cylinder in time dt is $\mathbf{J} \, dA \, dt$. But the force acting on unit electric charge in the direction of its motion is the component of $\mathbf{E}$ in this direction, since the magnetic force is always at right angles to its motion. Moreover the difference of electric potential between the two ends of the cylinder is $\mathbf{E}dl$. Hence the work done in the time dt on the

* See S; E. T. p. 131.

Cf. Guggenheim, *Proc. Roy. Soc.* A. 1936 **155** 49.

ʹelectricity while it is passing through this cylinder is $JdAdtEdl$ or $\mathbf{EJ}\,dV\,dt$, where dV is the element of volume.

It follows that the work $-w$ done by the whole system in the time dt is just equal to the first term of (5). Consequently we have

$$w = \int dV\,\mathbf{E}\,d\mathbf{D} + \int dV\,\mathbf{H}\,d\mathbf{B} \qquad\qquad 12A.\,6$$

The two terms on the right of (6) are naturally called *electrostatic work* and *magnetic work* respectively.

COMPARISON OF RATIONAL AND IRRATIONAL SYSTEMS

The following table shows how any quantitity in the rational system is translated into the corresponding quantity in the irrational system

Rational	Irrational
Q	Q
$\imath$	$\imath$
ψ	ψ
A	A
E	E
B	B
ε_0	$\varepsilon_0/4\pi$
μ_0	$4\pi\mu_0$
$\varepsilon_0\mu_0$	$\varepsilon_0\mu_0$
ε	$\varepsilon/4\pi$
μ	$4\pi\mu$
$\varepsilon\mu$	$\varepsilon\mu$
D	$D/4\pi$
H	$H/4\pi$
ED	$ED/4\pi$
BH	$BH/4\pi$

It is to be noted that the difference between the rational and irrational systems is a difference in the definition of certain quantities. It has nothing to do with the choice of units *. For example we have in the rational system

$$\varepsilon_0 = \frac{1}{4\pi}\frac{\text{franklin}^2}{\text{erg cm}} = 8.854 \times 10^{-12}\frac{C^2}{J\,m}$$

whereas in the irrational system

$$\varepsilon_0 = 1\frac{\text{franklin}^2}{\text{erg cm}} = 1.1126 \times 10^{-10}\frac{C^2}{J\,m}$$

* See Guggenheim, *Phil. Mag.* 1942 **33** 487

SPECIMEN IN UNIFORM EXTERNAL FIELD

We consider a uniform magnetic field inside an empty solenoid. We suppose that a specimen of isotropic matter is introduced into this field.

We use $\mathbf{B_e}$ to denote the force vector (induction) of the uniform field before the specimen is introduced, while $\mathbf{B}$, $\mathbf{H}$, $\mathbf{M}$ refer to the state with the specimen present. $\mathbf{M}$ of course vanishes outside the specimen. We define $\mathbf{H_e}$, $\mathbf{B_i}$, $\mathbf{H_i}$ by

$$\mathbf{B_e} = \mu_0 \mathbf{H_e} \qquad\qquad \text{12C. 1}$$

$$\mathbf{B} = \mathbf{B_e} + \mathbf{B_i}$$
$$= \mu_0 \left(\mathbf{H_e} + \mathbf{H_i} + \mathbf{M} \right) \qquad\qquad \text{12C. 2}$$

respectively.

The following conditions are obeyed

$$\text{div } \mathbf{B} = 0 \qquad \text{div } \mathbf{B_e} = 0 \qquad \text{div } \mathbf{B_i} = 0 \qquad \text{12C. 3}$$

$$\text{curl } \mathbf{H_i} = 0 \qquad \text{curl } (d\mathbf{H_i}) = 0 \qquad\qquad \text{12C. 4}$$

We shall prove that

$$w \equiv \int dV \, \mathbf{H} \, d\mathbf{B} - \int dV \, \mathbf{H_e} \, d\mathbf{B_e} = \int dV \, \mathbf{B_e} \, d\mathbf{M}$$

We have

$$w \equiv \int dV \, \mathbf{H} \, d\mathbf{B} - \int dV \, \mathbf{H_e} \, d\mathbf{B_e}$$

$$= \int dV \, \mathbf{H_i} \, d\mathbf{B} + \int dV \, \mathbf{H_e} \, d\mathbf{B_i} \qquad\qquad \text{12C. 5}$$

But owing to (3) and (4)

$$\int dV \, \mathbf{H_i} \, d\mathbf{B} = 0 \qquad\qquad \text{12C. 6}$$

and so

$$w = \int dV \, \mathbf{H_e} \, d\mathbf{B_i}$$

$$= \int dV \, \mathbf{H_e} \mu_0 \, d\mathbf{H_i} + \int dV \, \mathbf{H_e} \mu_0 \, d\mathbf{M}$$

$$= \int dV \, \mathbf{B_e} \, d\mathbf{H_i} + \int dV \, \mathbf{B_e} \, d\mathbf{M} \qquad\qquad \text{12C. 7}$$

Again from (3) and (4) there follows

$$\int dV \, \mathbf{B_e} \, d\mathbf{H_1} = 0 \qquad\qquad \text{12C. 8}$$

Consequently

$$w = \int dV \, \mathbf{B_e} \, d\mathbf{M} \qquad\qquad \text{12C. 9}$$

which was to be proved.

This elegant proof was supplied by Casimir *, who at the same time drew attention to an algebraic error in the first edition of this book.

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* Casimir, private communication.

RADIATION

§ 13. 01 GENERAL CONSIDERATIONS

There are several alternative ways of approach to the thermo-dynamics of radiation. We shall choose the one according to which the radiation is regarded as a collection of photons. Each photon is characterized by a frequency, a direction of propagation and a plane of polarization. In empty space all photons have equal speeds c. Each photon has an energy U_i related to its frequency ν_i by Planck's relation

$$U_i = h\nu_i \qquad\qquad 13.\,01.\,1$$

and a momentum of magnitude $h\nu_i/c$. It is convenient to group together all the species of photons having equal frequencies, and so equal energies, but different directions of propagation and planes of polarization. We denote by g_i the number of distinguishable kinds of photons having frequencies ν_i and energies U_i. More precisely $g_i\,d\nu_i$ denotes the number of distinguishable kinds of photons having frequencies between ν_i and $\nu_i + d\nu_i$ and energies between U_i and $U_i + dU_i$. By purely geometrical considerations it can be shown * that in an enclosure of volume V

$$g_i\,d\nu_i = 2 \times \frac{4\pi V}{c^3}\,\nu_i^2\,d\nu_i \qquad\qquad 13.\,01.\,2$$

the factor 2 being due to the two independent planes of polarization.

§ 13. 02 ENERGY AND ENTROPY IN TERMS OF g_i'S

We denote by N_i the number of photons having energies U_i and frequencies ν_i interrelated by (13. 01. 1). Then the total energy U is given by

$$U = \Sigma_i\,N_i\,U_i \qquad\qquad 13.\,02.\,1$$

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* See for example, Brillouin, *Die Quantenstatistik* 1931 chapter 2.
Fowler and Guggenheim, *Statistical Thermodynamics* 1939 §§ 401—403.

From the fact that photons obey Bose-Einstein statistics it can be shown * that the entropy S of the system is given by

$$\frac{S}{k} = \Sigma_i \ln \frac{(g_i + N_i)!}{g_i! \, N_i!} \qquad \text{13. 02. 2}$$

Differentiating (1) and (2) at constant g_i, that is to say constant V, we have

$$dU = \Sigma_i \, U_i \, dN_i \qquad \text{13. 02. 3}$$

$$\frac{dS}{k} = \Sigma_i \ln \frac{g_i + N_i}{N_i} \, dN_i \qquad \text{13. 02. 4}$$

The condition for equilibrium is according to (1. 43. 1) that S should be a maximum for given U, V. Hence for the most general possible variation, the expressions (3) and (4) must vanish simultaneously. It follows that

$$\frac{U_i}{\ln \dfrac{g_i + N_i}{N_i}} = \frac{U_k}{\ln \dfrac{g_k + N_k}{N_k}} \qquad \text{(all } i, k) \qquad \text{13. 02. 5}$$

and consequently by using (3) and (4)

$$\frac{U_i}{\ln \dfrac{g_i + N_i}{N_i}} = \frac{\Sigma_i \, U_i \, dN_i}{\Sigma_i \ln \dfrac{g_i + N_i}{N_i} \, dN_i} = k \frac{dU}{dS} = kT \qquad \text{13. 02. 6}$$

since at constant volume

$$dU = TdS \qquad \text{(const. } V) \qquad \text{13. 02. 7}$$

From (6) we have

$$\frac{N_i}{g_i + N_i} = e^{-U_i/kT} \qquad \text{13. 02. 8}$$

and so

$$N_i = \frac{g_i}{e^{U_i/kT} - 1} \qquad \text{13. 02. 9}$$

Substituting (9) into (1), we obtain

$$U = \Sigma_i \frac{g_i \, U_i}{e^{U_i/kT} - 1} \qquad \text{13. 02. 10}$$

* See for example, Brillouin, *Die Quantenstatistik* 1931 chapter 6.

For the entropy we obtain from (2), using Stirling's approximation for the factorials,

$$S = \Sigma_i \, N_i \ln \frac{g_i + N_i}{N_i} + \Sigma_i \, g_i \ln \frac{g_i + N_i}{g_i}$$

$$= \Sigma_i \frac{N_i U_i}{kT} - \Sigma_i \, g_i \ln (1 - e^{-U_i/kT}) \qquad \text{13. 02. 11}$$

by use of (8).

For the free energy F we deduce from (1) and (11)

$$F = U - TS = kT \, \Sigma_i \, g_i \ln (1 - e^{-U_i/kT}) \qquad \text{13. 02. 12}$$

§ 13. 03 THERMODYNAMIC FUNCTIONS

In the previous section we obtained formulae for the energy, entropy and free energy in terms of the U_i's and g_i's without making any use of (13. 01. 1) or (13. 01. 2). If we now substitute the values of U_i and g_i, given by these formulae, into the relations of the previous section we obtain

$$F = \frac{8\pi V}{c^3} \, kT \int_0^\infty \ln (1 - e^{-h\nu/kT}) \, \nu^2 \, d\nu \qquad \text{13. 03. 1}$$

$$U = \frac{8\pi V}{c^3} \int_0^\infty \frac{h\nu^3 \, d\nu}{e^{h\nu/kT} - 1}. \qquad \text{13. 03. 2}$$

We can write (2) in the form

$$U = \int_0^\infty U_\nu \, d\nu \qquad \text{13. 03. 3}$$

$$U_\nu = V \frac{8\pi}{c^3} \frac{h\nu^3}{e^{h\nu/kT} - 1} \qquad \text{13. 03. 4}$$

which is *Planck's formula* from which quantum theory originated.

§ 13. 04 EVALUATION OF INTEGRALS

We can rewrite (13. 03. 1) as

$$F = \frac{8\pi V k^4 T^4}{c^3 h^3} \, , \qquad \text{13. 04. 1}$$

where I is the integral defined by

$$I \equiv -\int_0^\infty \xi^2 \ln{(1 - e^{-\xi})} \, d\xi \qquad 13.\,04.\,2$$

Using the power series for the logarithm and then integrating term by term, we obtain

$$I = \int_0^\infty \sum_{n=1}^\infty \frac{\xi^2}{n} e^{-n\xi} \, d\xi = \sum_{n=1}^\infty \frac{1}{n^4} \int_0^\infty \eta^2 \, e^{-\eta} \, d\eta$$

$$= 2 \sum_{n=1}^\infty \frac{1}{n^4} = \frac{\pi^4}{45} \qquad 13.\,04.\,3$$

Substituting (3) into (1) we obtain finally

$$F = -\frac{8\pi^5 k^4}{45 c^3 h^3} \, T^4 V \qquad 13.\,04.\,4$$

§ 13.05 STEFAN-BOLTZMANN LAW

We could obtain formulae similar to (13.04.4) for U and S by evaluation of the relevant integrals, but it is more convenient to obtain these formulae by differentiation of (13.04.4).

We first abbreviate (13.04.4) to

$$F = -\tfrac{1}{3} a T^4 V \qquad 13.\,05.\,1$$

where a is a universal constant defined by

$$a = \frac{8\pi^5 k^4}{15 c^3 h^3} = 7.561 \times 10^{-15} \text{ erg cm}^{-3} \text{ deg}^{-4} \qquad 13.\,05.\,2$$

From (1) we deduce immediately

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = \tfrac{4}{3} a T^3 V \qquad 13.\,05.\,3$$

$$U = F + TS = a T^4 V \qquad 13.\,05.\,4$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \tfrac{1}{3} a T^4 = \tfrac{1}{3} \frac{U}{V} \qquad 13.\,05.\,5$$

$$G = F + PV = 0 \qquad 13.\,05.\,6$$

Formula (5) can be derived from classical electromagnetic theory.

Formula (4) was discovered by Stefan and derived theoretically by Boltzmann. It is called the *Stefan-Boltzmann law*.

From (4) we see that aT^4 is the equilibrium value of the radiation per unit volume in an enclosure. If a small hole is made in such an enclosure then it can be shown by geometrical considerations that the radiation emitted through the hole per unit area and per unit time is σT^4, where σ is given by

$$\sigma = \tfrac{1}{4}ac = 5.667 \times 10^{-5} \text{ erg cm}^{-2} \text{ s}^{-1} \text{ deg}^{-4} \qquad 13.\,05.\,7$$

in which c denotes the speed of light. This constant σ is called the *Stefan-Boltzmann constant*.

§ 13. 06 ADIABATIC CHANGES

Suppose radiation is confined by perfectly reflecting walls and the volume of the container is altered by moving a piston. If the radiation remains in thermal equilibrium its temperature will change. For such a reversible adiabatic change, we have

$$S = \text{const.} \qquad 13.\,06.\,1$$

From (13. 05. 3) and (1) it follows that

$$VT^3 = \text{const.} \qquad \text{(adiabatic)} \qquad 13.\,06.\,2$$

From (13. 05. 4) and (13. 05. 5) we have

$$P/T^4 = \text{const.} \qquad 13.\,06.\,3$$

so that $\qquad\qquad PV/T = \text{const.} \qquad \text{(adiabatic)} \qquad 13.\,06.\,4$

and $\qquad\qquad PV^{\frac{4}{3}} = \text{const.} \qquad \text{(adiabatic)} \qquad 13.\,06.\,5$

From (2), (3), (4), (5) it appears that the relations for a reversible adiabatic change in radiation are formally similar to those for a perfect gas such that the ratio C_P/C_V has the constant value $\tfrac{4}{3}$. This apparent resemblance is however accidental, for the ratio C_P/C_V of radiation is not $\tfrac{4}{3}$. In fact for radiation

$$\left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V = 4aT^3V \qquad 13.\,06.\,6$$

while

$$T\left(\frac{\partial S}{\partial T}\right)_P = \infty \qquad 13.\,06.\,7$$

since no increase in S, however great, can increase T without increasing P.

ONSAGER'S RECIPROCAL RELATIONS

§ 14. 01 INTRODUCTION

We recall the fundamental properties of entropy stated in § 1. 17. The entropy of a system can change in two distinct ways namely by external and internal changes. This is expressed symbolically by

$$dS = d_eS + d_iS \qquad 14.01.1$$

where d_eS denotes the part of dS due to interaction with the surroundings and d_iS denotes the part due to changes taking place in the system. We have the now familiar equality

$$d_eS = \frac{q}{T} \qquad 14.01.2$$

where T is the absolute temperature of the system. As regards d_iS the only property hitherto stressed is the inequality

$$d_iS > 0 \qquad 14.01.3$$

We shall in this chapter consider more quantitatively the value of d_iS or rather of d_iS/dt which is the rate of internal production of entropy. Such considerations constitute a subject often called *thermodynamics of irreversible processes*. It is a subject on which whole books * have been written and it is not practicable to devote sufficient space here for an exhaustive discussion. For the sake of brevity it has been decided to confine the present discussion to isothermal systems. This means exclusion of two important and interesting fields, thermal diffusion and thermoelectricity. The reader interested in these phenomena must turn to one of the monographs devoted to irreversible processes.

Although the present treatment is restricted to isothermal systems, it is adequate for illustrating the general principles. It will be applied to two important fields, electrokinetic phenomena and electrochemical cells with transference.

* De Groot, *Thermodynamics of Irreversible Processes* 1951.
Denbigh, *The Thermodynamics of the Steady State* 1951.
Prigogine and Defay, *Etude Thermodynamique des Phénomènes Irréversibles* 1947.

§ 14. 02 ELECTRIC INSULATORS AND CONDUCTORS

We shall introduce the subject of internal entropy production by considering electric conductors which we shall compare and contrast with electric insulators. We begin with the simplest case of isotropic media and then pass on to the much more interesting case of anisotropic media.

The free energy F of an electric insulator is related to the electric field $\mathbf{E}$ and the electric displacement $\mathbf{D}$, under isothermal conditions, by

$$\frac{\mathrm{d}F}{V} = \mathbf{E}\mathrm{d}\mathbf{D} \qquad 14.\,02.\,1$$

This follows immediately from formula (12. 07. 1) but differs from the formulae of chapter 11 by the omission of a factor $1/4\pi$ because we are here using the rational system described in chapter 12. We recall that $\mathbf{D}$ is related to $\mathbf{E}$ by

$$\mathbf{D} = \varepsilon\mathbf{E} \qquad 14.\,02.\,2$$

where ε is the permittivity. Under ordinary conditions ε is independent of $\mathbf{E}$ and this will be assumed.

In an isotropic medium $\mathbf{D}$ and $\mathbf{E}$ have the same direction and ε is a scalar quantity. In an anisotropic medium $\mathbf{D}$ and $\mathbf{E}$ generally have different directions. A quantity such as ε relating two non-parallel vectors $\mathbf{D}$ and $\mathbf{E}$ according to (2) is called a tensor. Without any prior knowledge of tensors we can see what this means by considering the cartesian components of (2). The relations for these components have the form

$$D_x = \varepsilon_{xx}E_x + \varepsilon_{xy}E_y + \varepsilon_{xz}E_z \qquad 14.\,02.\,3$$

$$D_y = \varepsilon_{yx}E_x + \varepsilon_{yy}E_y + \varepsilon_{yz}E_z \qquad 14.\,02.\,4$$

$$D_z = \varepsilon_{zx}E_x + \varepsilon_{zy}E_y + \varepsilon_{zz}E_z \qquad 14.\,02.\,5$$

where all the quantities are scalars.

Since we are assuming that ε is independent of $\mathbf{E}$, we can substitute (2) into (1) and integrate obtaining, apart from a trivial integration constant,

$$F = \tfrac{1}{2}\varepsilon\mathbf{E}^2 \qquad 14.\,02.\,6$$

In an isotropic medium ε is as we have already mentioned a scalar and there is no difficulty. In an anisotropic medium the meaning of (6) is by no means so simple and its interpretation requires at least an

elementary knowledge of tensors. However all that we need to record here is that the existence of the free energy F related to **E** and **D** by (1) requires the symmetry conditions

$$\varepsilon_{xy} = \varepsilon_{yx} \qquad \varepsilon_{yz} = \varepsilon_{zy} \qquad \varepsilon_{zx} = \varepsilon_{xz} \qquad \text{14. 02. 7}$$

In the terminology of tensors we say that ε must be a symmetrical tensor. When the relations (7) are assumed, the expression for the free energy becomes

$$F = \tfrac{1}{2}\varepsilon_{xx} E_x^2 + \tfrac{1}{2}\varepsilon_{yy} E_y^2 + \tfrac{1}{2}\varepsilon_{zz} E_z^2$$
$$+ \varepsilon_{xy} E_x E_y + \varepsilon_{yz} E_y E_z + \varepsilon_{zx} E_z E_x \qquad \text{14. 02. 8}$$

When we assume (8) and (7) we can immediately derive (3), (4) and (5) by means of (1). Without the relations (7) it is impossible to find any formula for F consistent with (1).

We now turn from insulators to conductors. If we denote electric field by **E** and current density by **J** we may write

$$\mathbf{J} = \sigma \mathbf{E} \qquad \text{14. 02. 9}$$

where σ denotes the electric conductivity. Under ordinary conditions σ is independent of **E** and we shall assume this. In an isotropic medium **J** and **E** have the same direction and σ is a scalar quantity. In an anisotropic medium **J** and **E** generally have different directions so that σ is a tensor. The relations between the cartesian components have the form

$$J_x = \sigma_{xx} E_x + \sigma_{xy} E_y + \sigma_{xz} E_z \qquad \text{14. 02. 10}$$

$$J_y = \sigma_{yx} E_x + \sigma_{yy} E_y + \sigma_{yz} E_z \qquad \text{14. 02. 11}$$

$$J_z = \sigma_{zx} E_x + \sigma_{zy} E_y + \sigma_{zz} E_z \qquad \text{14. 02. 12}$$

where all the quantities are scalars.

Let us now determine the rate of internal production of entropy in the simple case of an isotropic medium so that **J** has the same direction as **E**. It is simplest to assume that the conductor is maintained at a constant temperature and that **J** and **E** are independent of the time. The conductor is then maintained in an unchanging state so that

$$\frac{dS}{dt} = 0 \qquad \text{14. 02. 13}$$

Substituting from (14. 01. 1) and (14. 01. 2) into (13) we obtain

$$\frac{d_i S}{dt} = \frac{d_e S}{dt} - \frac{1}{T}\frac{dq}{dt} \qquad \text{14. 02. 14}$$

where $-q$ is the heat given up to the thermostat. From elementary electrical theory we have

$$-\frac{1}{V}\frac{dq}{dt} = \mathbf{JE} \qquad \text{14. 02. 15}$$

Substituting (15) into (14) we obtain

$$\frac{T}{V}\frac{d_i S}{dt} = \mathbf{JE} \qquad \text{14. 02. 16}$$

Finally substituting (9) into (16) we obtain

$$\frac{T}{V}\frac{d_i S}{dt} = \sigma\mathbf{E}^2 \qquad \text{14. 02. 17}$$

In the more complicated and more interesting case of an anisotropic conductor, we obtain by similar but more difficult reasoning

$$\frac{T}{V}\frac{d_i S}{dt} = J_x E_x + J_y E_y + J_z E_z \qquad \text{14. 02. 18}$$

Substituting (10), (11) and (12) into (18) we derive

$$\begin{aligned}
\frac{T}{V}\frac{d_i S}{dt} = {} & \sigma_{xx} E_x^2 + \sigma_{yy} E_y^2 + \sigma_{zz} E_z^2 \\
& + (\sigma_{xy} + \sigma_{yx})\, E_x E_y + (\sigma_{yz} + \sigma_{zy})\, E_y E_z \\
& + (\sigma_{zx} + \sigma_{xz})\, E_z E_x
\end{aligned} \qquad \text{14. 02. 19}$$

If we compare (19) with (8) we notice a superficial resemblance but also two differences which are interrelated. In the first place F occurring on the left of (8) is a function of the state of the medium while $d_i S/dt$ occurring on the left of (19) is not. In the second place, and as a consequence of the first difference, there is no compelling reason from classical thermodynamics for relations between the σ's analogous to the relations (7). There are however reasons based on the kinetic principle of detailed balancing,[*] which we shall not here go into, for assuming

$$\sigma_{xy} = \sigma_{yx} \qquad \sigma_{yz} = \sigma_{zy} \qquad \sigma_{zx} = \sigma_{xz} \qquad \text{14. 02. 20}$$

[*] Onsager *Phys. Rev.* 1931 **37** 405.
See also De Groot, *Thermodynamics of Irreversible Processes* 1951.

and such relations are in good agreement with experiment. The equations (20) constitute one of the simplest examples of *Onsager's reciprocal relations*.

§ 14.03 ONSAGER'S RECIPROCAL RELATIONS

We are now ready for a more general statement of Onsager's reciprocal relations. We denote by J_i the flux in a certain direction of something such as electric charge, as in the previous section, or a particular molecular or ionic species or a quantity of energy. We denote by X_i the *driving force* corresponding to J_i. We make our meaning more precise by the statement that the rate of internal production of entropy per unit volume is given by

$$\frac{T}{V}\frac{\mathrm{d}_i S}{\mathrm{d}t} = \Sigma_i J_i X_i \qquad\qquad 14.03.1$$

For example when J_i is electric current density, then X_i is the electric field. When J_i is the flux of a molecular species i, then X_i is minus the gradient of its chemical potential. When J_i is the flux of an ionic species i, then X_i is minus the gradient of its electrochemical potential. When J_i is the flux of energy then X_i must be closely related to the temperature gradient, but, as already mentioned, we shall not here consider non-isothermal systems.

Provided the gradients X_i are not too great the fluxes J_i will generally be linear functions of the driving forces. This may be expressed as

$$J_i = \Sigma_k L_{ik} X_k \qquad (L_{ik}\ \text{const.}) \qquad 14.03.2$$

In the simple case of only two kinds of flow (2) reduces to

$$J_1 = L_{11}X_1 + L_{12}X_2 \qquad\qquad 14.03.3$$

$$J_2 = L_{21}X_1 + L_{22}X_2 \qquad\qquad 14.03.4$$

We now state Onsager's reciprocal relations in the general form

$$L_{ik} = L_{ki} \qquad (\text{all } i, k) \qquad\qquad 14.03.5$$

In the simple case of only two kinds of flow (5) reduces to

$$L_{12} = L_{21} \qquad\qquad 14.03.6$$

§ 14.04 ELECTROKINETIC EFFECTS

Electrokinetic phenomena occur when a liquid, which is a poor electric conductor, flows through a tube. Generally the tube walls and the liquid have opposite electric charges together constituting an electric double layer. There is a consequent interplay between the flow of matter and the flow of electric charge.

We consider a tube of length l and uniform cross-section A. We denote the electric current density by $\mathbf{J}$ and the electric field, which is equal and opposite to the electric potential gradient, by $\mathbf{E}$. We measure the rate of flow of liquid as the volume per unit time and we denote this by f. We denote the pressure difference between the ends of the tube by P. It can be verified that the rate of internal production of entropy per unit volume is given by

$$\frac{T}{V} \frac{d_i S}{dt} = \mathbf{J}\mathbf{E} + \frac{fP}{Al} \qquad 14.04.1$$

From the form of (1) we see that we may regard $\mathbf{E}$ and P/l as the driving forces corresponding to the fluxes $\mathbf{J}$ and f/A respectively. We assume the linear relations

$$\mathbf{J} = L_{11}\mathbf{E} + L_{12}\frac{P}{l} \qquad 14.04.2$$

$$\frac{f}{A} = L_{21}\mathbf{E} + L_{22}\frac{P}{l} \qquad 14.04.3$$

We then have Onsager's reciprocal relation

$$L_{12} = L_{21} \qquad 14.04.4$$

Let us now consider briefly the physical significance of the L's. In the absence of a pressure gradient (2) reduces to

$$\mathbf{J} = L_{11}\mathbf{E} \qquad (P = 0) \qquad 14.04.5$$

from which we see that L_{11} is just the electric conductivity. In the absence of an electric field (3) reduces to

$$\frac{f}{A} = L_{22}\frac{P}{l} \qquad 14.04.6$$

from which we have according to Poiseuille's law

$$L_{22} = \frac{r^2}{8\eta} \qquad 14.04.7$$

where η is the viscosity and r the radius of the tube (or the effective radius if the cross-section is not circular).

The essential consequence of Onsager's relation is this. All the electrokinetic effects require for their quantitative description a knowledge of the electric conductivity, the viscosity and *one other* coefficient, not two. We shall now formulate briefly the relations for some of the most important electrokinetic effects.*

In the first place we have the *streaming potential* defined as the electric potential difference per unit pressure difference in a stationary state with zero electric current. According to (2) it is given by

$$\frac{l\mathbf{E}}{P} = -\frac{L_{12}}{L_{11}} \qquad (\mathbf{J} = 0) \qquad 14.\,04.\,8$$

In the second place we have *electro-osmosis* which is the flow of liquid per unit electric current in a state with zero pressure gradient. According to (2) and (3) it is given by

$$\frac{f}{\mathbf{J}A} = \frac{L_{21}}{L_{11}} \qquad (P = 0) \qquad 14.\,04.\,9$$

The third effect is the *electro-osmotic pressure* which is the pressure difference per unit potential difference in the stationary state with zero material flow. According to (3) it is given by

$$\frac{P}{\mathbf{E}l} = -\frac{L_{21}}{L_{22}} \qquad (f = 0) \qquad 14.\,04.\,10$$

The fourth effect is the *streaming current* which is the electric current per unit material flow for the steady state of zero electric field. According to (2) and (3) it is given by

$$\frac{\mathbf{J}A}{f} = \frac{L_{12}}{L_{22}} \qquad (\mathbf{E} = 0) \qquad 14.\,04.\,11$$

§ 14. 05 ELECTRIC DOUBLE LAYER

We have seen in the previous section how the several electrokinetic effects can be expressed quantitatively in terms of the conductivity, the viscosity and one further parameter denoted by L_{12}. It was not necessary to consider the physical significance of L_{12}. We shall now show that this quantity is closely related to the strength of the electric

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* De Groot, *Thermodynamics of Irreversible Processes* 1951 p. 187.

double layer at the boundary between the wall of the tube and the liquid in the tube. It does not matter which of the electrokinetic effects we consider in order to establish the required relation. We choose to consider electro-osmosis.

We consider a thin strip of liquid near to and parallel to the wall. We denote by du the difference of velocity along the tube between the inner and outer surface of this strip. We denote by $d\tau$ the strength of the electric double layer in this strip, that is to say the electric moment per unit area of the strip. We consider a steady state of motion under an applied electric field $\mathbf{E}$. We now equate the two opposing couples due to the viscous effect of the velocity gradient on the one hand and the effect of the electric field on the dipoles on the other. We thus obtain the condition

$$\eta\,du = \mathbf{E}\,d\tau \qquad\qquad 14.\,05.\,1$$

Integrating from the wall, where the liquid is stationary, to the interior we obtain for the velocity u in the interior of the liquid

$$\eta u = \mathbf{E}\tau \qquad\qquad 14.\,05.\,2$$

where τ is the strength of the whole double layer, that is to say the total electric moment per unit area of the wall.

The flow f expressed as volume of liquid per unit time is given by

$$f = uA \qquad\qquad 14.\,05.\,3$$

where A is an area less than the total internal cross-section of the tube but greater than the cross-section of liquid having a velocity inappreciably different from u. In practice the thickness of the double layer is small compared with the width of the tube and consequently the difference between these cross-sections is negligible. We may then regard A as the internal cross-section of the tube. Substituting (2) into (3) we have

$$\frac{f}{A} = \frac{\tau\mathbf{E}}{\eta} \qquad\qquad 14.\,05.\,4$$

while from (14. 04. 3) we have

$$\frac{f}{A} = L_{21}\mathbf{E} \qquad (P = 0) \qquad 14.\,05.\,5$$

Comparing (4) with (5) we deduce

$$L_{21} = \frac{\tau}{\eta} \qquad\qquad 14.\,05.\,6$$

Formula (6) expresses a relation essentially due to Helmholtz[*] although he did not use the same notation. Most authors instead of using Helmholtz' strength of the double layer here denoted by τ prefer to consider another quantity introduced by Perrin[†] and subsequently denoted by ζ by Freundlich[§]. This quantity has the dimensions of an electric potential and is called the ζ potential. It is derived from τ by division by the rational permittivity. In the author's opinion the introduction of this subsidiary quantity adds nothing except unnecessary complication.[‡]

§ 14. 06 ELECTROCHEMICAL CELLS WITH TRANSFERENCE

We shall now use Onsager's reciprocal relations to obtain a stricter derivation of formula (9. 18. 16) for the electromotive force of the cell with transference described by (9. 18. 2). We shall not repeat the whole of the textual argument, but shall merely revise the formulae. The first change is that we replace (9. 18. 3) by the less restrictive assumption

$$J_i = -\Sigma_k L_{ik} \frac{d\mu_k}{dy} \qquad 14.\,06.\,1$$

The condition for zero electric current then becomes instead of (9. 18. 9)

$$\Sigma_i \Sigma_k z_i L_{ik} \frac{d\mu_k}{dy} = 0 \qquad 14.\,06.\,2$$

We still have for the electromotive force formula (9. 18. 7)

$$F \frac{dE}{dy} = \frac{1}{z_{Cl^-}} \frac{d\mu_{Cl^-}}{dy} \qquad 14.\,06.\,3$$

Combining (2) with (3) we have

$$\Sigma_i \Sigma_k z_i z_k L_{ik} \left(-\frac{1}{z_k} \frac{d\mu_k}{dy} + \frac{1}{z_{Cl^-}} \frac{d\mu_{Cl^-}}{dy} \right)$$

$$= \Sigma_i \Sigma_k z_i z_k L_{ik} \frac{1}{z_{Cl^-}} \frac{d\mu_{Cl^-}}{dy}$$

$$= \Sigma_i \Sigma_k z_i z_k L_{ik} F \frac{dE}{dy} \qquad 14.\,06.\,4$$

[*] Helmholtz, *Ann. Phys., Lpz.* 1879 **7** 337.
[†] Perrin, *J. Chim. Phys.* 1904 **2** 601.
[§] Freundlich, *Colloid and Capillary Chemistry* 1926 p. 242.
[‡] Guggenheim, *Trans. Faraday Soc.* 1940 **36** 139 722.

Consequently

$$F\frac{dE}{dy} = \Sigma_k \left\{ \left(-\frac{1}{z_k}\frac{d\mu_k}{dy} + \frac{1}{z_{Cl^-}}\frac{d\mu_{Cl^-}}{dy} \right) \left(\frac{z_k \Sigma_i z_i L_{ik}}{\Sigma_l \Sigma_m z_l z_m L_{lm}} \right) \right\} \qquad 14.06.5$$

instead of (9.18.11).

We now, as in § 9.18, turn to the different condition where the two electrode solutions are identical and an external potential difference dE^e is applied across the electrodes. We have by (9.18.12)

$$\frac{1}{z_k}d\mu_k = F dE^e \qquad \text{(all } k\text{)} \qquad 14.06.6$$

so that by (1)

$$J_l = -\Sigma_k z_k L_{ik} F\frac{dE^e}{dy} \qquad 14.06.7$$

The electric current per unit cross-section carried by the ionic species i will be

$$z_i F J_i = -z_i \Sigma_k z_k L_{ik} F^2 \frac{dE^e}{dy} \qquad 14.06.8$$

The transport number t_i being the fraction of the total current carried by the ionic species i is therefore

$$t_i := \frac{z_i \Sigma_k z_k L_{ik}}{\Sigma_i \Sigma_k z_i z_k L_{ik}} \qquad 14.06.9$$

The transport number of the ionic species k is likewise

$$t_k = \frac{z_k \Sigma_i z_i L_{ki}}{\Sigma_k \Sigma_i z_k z_i L_{ki}}$$

$$= \frac{z_k \Sigma_i z_i L_{ki}}{\Sigma_l \Sigma_m z_l z_m L_{lm}} \qquad 14.06.10$$

Comparing (5) with (10) we have

$$F\frac{dE}{dy} = \Sigma_k t_k \left(-\frac{1}{z_k}\frac{d\mu_k}{dy} + \frac{1}{z_{Cl^-}}\frac{d\mu_{Cl^-}}{dy} \right) \frac{\Sigma_i z_i L_{ik}}{\Sigma_i z_i L_{ki}} \qquad 14.06.11$$

Finally by use of Onsager's relation

$$L_{ik} = L_{ki} \qquad \text{14. 06. 12}$$

(11) reduces to

$$F \frac{dE}{dy} = \Sigma_k t_k \left(-\frac{1}{z_k} \frac{d\mu_k}{dy} + \frac{1}{z_{Cl^-}} \frac{d\mu_{Cl^-}}{dy} \right) \qquad \text{14. 06. 13}$$

which is the same as formula (9. 18. 16).

We note that in the derivation given in § 9. 18 instead of Onsager's relation (12) we used the more restrictive and unjustifiable assumption $L_{ik} = 0$ except when i and k are identical.

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